CHEMISTRY IN INDUSTRY

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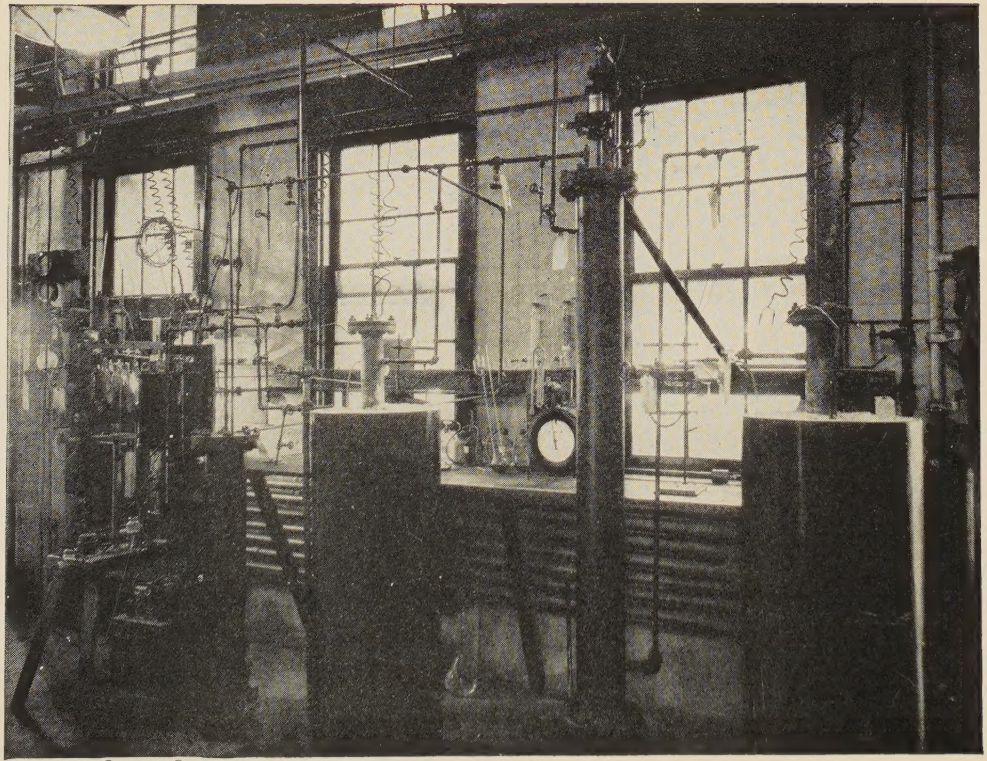

Courtesy, Lazote, Inc.

Catalyst Testing Plant

Low-pressure purification train showing ammonia cracker, water scrubber, and deoxidizer. Ammonia is cracked to give the necessary pure nitrogen and hydrogen. The purpose of the plant is to determine the efficiency of various ammonia catalysts under different conditions of temperature and pressure.

CHEMISTRY IN INDUSTRY

A COÖPERATIVE WORK INTENDED TO GIVE EXAMPLES OF THE CONTRIBUTIONS MADE TO INDUSTRY BY CHEMISTRY

EDITED BY

H. E. HOWE

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CHEMISTRY IN INDUSTRY

VOLUME II

Preface

When the first volume of Chemistry in Industry, now in its thirtieth thousand, was published, it was with a view to providing a convenient source of information relative to the part played by chemistry in a few selected industries. The need for such a reference work had been discovered in administering the Prize Essay Contest of the American Chemical Society, in which competition a number of those who preferred to discuss the relation of chemistry to an industry or natural resource had difficulty in obtaining data easy to read and comprehensible to those who had not specialized in chemical studies.

Business executives and financiers close to industry have found Chemistry in Industry appealing beyond the anticipation of those responsible for Volume I. It was not foreseen that many copies of the first volume would be found useful in presenting to possible subscribers to research and other educational funds an appeal based upon the earning power of chemistry. Those responsible for the compilation and publication of Volume I have been gratified to find how extensive a service can be rendered by a volume of that type, and in view of the facts it is not surprising to find a demand for further chapters dealing with industries that could not be included in the first book. Not only

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have those who read Volume I inquired for Volume II, but the industries themselves have asked in many cases for a place in a second volume of Chemistry in Industry.

It is therefore to meet this continued demand that Volume II has been undertaken. Once more certain industries have been selected for treatment, with the full knowledge that again important industries where chemistry plays a major part had to be omitted. But it is hoped that the chapters here presented will contain many points of real interest and constitute in the mind of the reader further proof, if it be needed, that chemistry, both in its research and applied phases, is fundamental to industrial success.

In the short time since Volume I appeared there have been a number of inspiring examples of chemistry at work in industry. The old-time varnish industry has found a new competitor in chemical compounds of cellulose in solvents, unknown outside the laboratory a short while ago, but now of such importance that they even have their influence upon the stock exchange. The wood distillation industry of the world, in which one hundred million dollars is estimated to be invested in America alone, has been brought face to face with a synthetic wood alcohol, or methanol as it is now known, said to be produced at a cost less than 20 per cent of that of the natural product. There has been a great increase in the use of synthetic resin. New rust-resisting metals have found their way upon the market. In the field of medicine the work of concentrating materials like insulin, so that smaller quantities might be as potent as the larger injections, has made progress and work continues on the chemistry of the all-important ductless glands and their secretions.

Profiting by the experience of the citrus growers, whose by-product plant is a great factor in the stabilization of the market, the raisin growers have perfected a fruit sirup which will not only utilize cull raisins, stems, etc., but at times of excess crops may be useful as an outlet for even marketable fruit. Since Volume I was issued, Baly has shown that a form of glucose can be derived from formaldehyde with the aid of ultra-violet light. Government bureaus have suggested that the mammoth white French Jerusalem artichoke may be found an important economic source of levulose, a nutritious and easily digested sugar. Many new colors have been perfected in America and offered on our markets. The artificial silk or rayon industry has grown by leaps and bounds. Court decisions have shown a better understanding of the relationship of chemistry to industry, health, and national defense. The press of the country has devoted an increasing amount of space to authoritative chemical stories, and radio managers sensing the interest of the public have been glad to broadcast stories of the chemist at work.

We would fail in discharging our duties, therefore, if we did not do our utmost to bring to the public in a form which it can easily understand such information regarding chemistry in its several relations as we know will eventually create a sympathetic appreciation of the work in hand. Many of the results recounted in this book would have been impossible but for the application of principles discovered through fundamental research, the sole object of which is the establishment of truth. In the last analysis it is to this type of work, the returns from which are often too impatiently awaited by stockholders, boards of directors,

and bankers, that we are indebted for the present high level of our civilization.

We can say with Aristotle (Met. A. 10: 993. A. 30), "The search for truth is in one way hard and in another easy. For it is evident that no one can master it fully nor miss it wholly. But each adds a little to our knowledge of nature, and from all the facts assembled there arises a certain grandeur."

Those who have generously contributed the chapters to Volume II are to be credited with any success which may come to it. And again appreciation is expressed for the help of those who have attended to all the numerous details incident to the compilation of a work of this character and seeing it through the press.

H. E. Howe,
Editor.

CHEMISTRY IN INDUSTRY

VOLUME II

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CHEMISTRY IN INDUSTRY

CHAPTER I

CATALYSIS—A NEW FACTOR IN INDUSTRY

ELLWOOD HENDRICK

Curator, Chandler Chemical Museum, Columbia University

Chemistry is much broader and bigger than what we can see or hear or feel or taste or smell. It is an aspect of the universe, and if we have not a sense of chemistry we are mentally blind; we cannot see with the eyes of the mind which imagination vouchsafes us, how and why things happen; how and why changes take place. Every plant, every animal, every living thing is a chemical phenomenon, and all gases and liquids and solids on the earth and in it and in the cosmic dust and far off in the starry heavens are first of all chemicals. The world is full of romance and of riddles; but when we let our imagination be guided by scholarship, clear beyond the realms that are familiar to us, way off into the invisible, inaudible, unfeelable realm of things almost infinitely minute, we meet familiar things again.

We think of our earth as a great ball revolving around the sun and we see the reflected light of the sun on other planets, so that in time we conceive an idea of our own solar system; of the comparatively small star ninety-odd million miles away that is the nucleus of our unit or system of the universe and of what it holds in gravitational leash. Then when we come to consider atoms, which are the smallest particles of any

of the eighty-odd elements, we find in each atom what seems to be a similar solar system, with a nucleus of positive charges of electricity in the center, and whirling round and round about it a given number of negative charges or electrons that behave like so many planets. And yet they are so small as to strain the imagination, so small that if we were to set all the inhabitants of the earth to counting the atoms in a cubic centimeter of air—a mere thimbleful in which they are not at all crowded together—and were to have all the people count three a second continuously, working day and night, it would take them years to finish the job. If we look hard enough, with the eyes of our minds, we seem to sense a certain uniformity of system in all the infinities, in the great and in the small, and even in the ways of people and of things.

We used to think that in the chemical elements we had reached the rock-bottom of the concept of matter, and that the elements were everlasting and eternal. We gave names to the elements, and one reason why chemistry often seems difficult to the beginner is because our emphasis on the names of things has made the gateway to science as pleasant and alluring as the multiplication table—but hardly more so. Now, following profounder study, it seems as though even the elements themselves—surely it may be said of a considerable number of them—are but temporary stages in the cosmic history of matter. Matter seems to be in process of creation today, in the sun and in the stars, actually coming into being under conditions of temperature and pressure that we cannot reach either physically or chemically, just as was going on when this earth was hurled forth into space, a seething clod of cosmic stuff. And disintegration is going on continually on the earth, in planets, and in moons and satel-

lites here and in systems hundreds of thousands of light years away. Thus matter goes back into positive and negative charges of electricity, into protons and electrons, out of which all matter appears to be composed, and then is shot off into space—who knows but to participate in creation again? A stupendous and bewildering continuum!

We—little wisps of consciousness that we are, here today and gone tomorrow—have missed these concepts because of the shortness of our lives. We have been too willing and ready to call things everlasting because we could not see the beginning or the end; too much disposed to confuse even geologic ages with eternity. The philosophy of chemistry teaches us humility. And remember this: the more we study, the more we understand, and the loftier the heights we scale, the greater are the mysteries beyond.

The Catalyst—A Self-Starter

We need not, however, strive for the outermost reaches of the imagination to find familiar things in chemistry. There is, for instance, catalysis, which is one of the most human manifestations of matter. How often has it not happened to the reader of this chapter, as well as to the writer, that we have been somewhere with friends and having a dull time of it. We have met, let us say, to draw up a set of resolutions, but we can't get much further than "Whereas!" Now "Whereas" makes a good formal beginning, but we did not invent it; we merely remember it, and that is easy. Not one of us is worth his salt at thinking up what to say. Each one wishes someone else would write the thing, because none of us feels like it. Then along comes another member of the committee who is not suf-

fering from our disabilities; he thinks we should have our resolutions drawn up by the time he arrives; to him the whole thing is very easy and he suggests merely a couple of whereases for a beginning. His presence, his voice, but more probably his energy, change us, and within five minutes we are all busy with suggestions, so that before twenty minutes more have passed we have our set of resolutions that fairly sing, all written out!

Or, it may be that with no specific purpose other than mutual entertainment we are making a failure of it, all sitting in a ring, gloomy and sour. Then in comes the catalyst, cracks a few jokes, tells one on himself, is evidently glad to be there, and straightway we catch his spirit and engage in active talk, enjoying ourselves and counting the occasion a rare one. Merely because the catalyst came in we have been changed from dull company into brilliant. How did it all happen? What did he do? Well, he catalyzed us, but we can write down every gesture he made and every word he said without explaining it.

Chemistry—A Catalyst Itself

Now chemistry changes industry in just that way, and when we get into chemistry we find catalysis, these sudden changes that take place in the presence of a sometimes exceedingly minute quantity of a seemingly foreign substance without which we cannot succeed in our undertaking.

As an example of how chemistry changes industry, let us recall the story of several brothers whose father and grandfather had made soap, good laundry soap. They had a "formula" and good foremen and they

made a decent living. The boys went to college, thanks to their father's provident habits and his ambition for them, and by the time they were back home again and getting to work the father died. Then they talked things over. Each was ambitious for himself, and while the business was big enough to provide for one family, here were several in prospect and the head of each hoping to be a man of consequence and to live well. Should one take over the establishment and the others seek other occupations, or should they make the business big enough to take care of them all? They decided on the latter course, and their first step was to find a competent chemist to introduce scientific control into the works. Soon they were using vegetable fats along with beef suet and mutton tallow; they ceased to produce by rule of thumb; they began to buy on specification and to manufacture under control. They added new products; the firm became a leader in quality goods and now it is an immense concern with world-wide ramifications. It was chemistry along with good business acumen that made the change. They never could have grown if they had stuck to the old methods.

Chemistry has only begun its work in industry, and it has much more to do than it has done thus far. We are still back in the middle ages in the way we produce iron, despite our big blast furnaces. Think, for instance, of the excessive heat required to warm up four volumes of nitrogen for every volume of oxygen that is needed hot. Or, if the ironmaster protests that the hot nitrogen helps him in his blast furnace, let's remember that theoretically and on a small scale it is possible to separate iron from its ore without either coke or limestone. It is the chemical engineer's business to turn the theoretical into the practical, and this

is still awaiting development. Enough support of research with the right men might easily bring it about.

Again, the farmer buys fertilizer by the ton, paying excess freight on 60 to 80 per cent of useless material, and when he gets it he does not know what the functions of the various ingredients of the mixture are. Chemistry has got in far enough to tell the farmer that he is getting the equivalent of so many pounds of ammonia, so many pounds of phosphoric acid anhydride, and so many pounds of potassium oxide per ton, but that is only a little fraction of what he needs to know. He has learned the chemical names, but he has not learned what's what.

This is no indictment of the iron or steel or fertilizer industries. It is told to show that when we look with the eye of science, we find it no virtue to be "up to date!" To be up to date is to follow the donkey path, or, to express ourselves more exactly, to be informed as to what living men have added to the work of the dead and to be equipped to profit by it. But chemistry looks way ahead and seeks to build up the great store of knowledge so that the present generation may do better than it is doing now, as well as better than those who have gone before, and so that men and women of the future may do better than we do. Any man who is satisfied with being merely up to date is not fit to administer a chemical industry—and every industry is more or less a chemical industry. The only safe place is ahead of the game.

A number of years ago two gentlemen were traveling from Boston to New York and they had dinner together on the train. One was head of a great department store and the other was a well-known chemist. "I am one of those persons," said the merchant, "whose business your profession does not touch!"

"I'd like to try," said the chemist. "In fact, if you will let me make a report on your store, and if you cannot save more than my fee every year, I'll provide the best dinner I can for you. And if you find that my examination of your place has been really worth while, then you can pay for the dinner." It was agreed, and the survey showed how, by buying on specification paper, twine, soap, cleansing powders and all such odds and ends, every one essentially a chemical product, the annual saving would be more than four times the chemist's fee. The merchant paid for the dinner.

We waste most of the lumber we cut, which chemistry could save. Of course, such things can't be done by a mere twist o' the wrist. We are not blaming the lumbermen because they don't do what might be done. We might be found a little shy ourselves along similar lines. It takes time and patience to work out such things, and then it takes courage to test them out.

Chemistry in Business

"To a certain extent, yes," as the king of bores says in reply to almost any question. There is the ghost of an indictment, or at least a warrant for a citation to show cause, that might be justly issued against American business in the matter of chemistry. Our corporation traditions provide that groups of investors be represented on boards of directors. The president is made a member, and the head of the sales department is likely to be added because the other members, consisting of bankers and merchants and a lawyer or so, can all understand what he says. The chief chemist is likely to be a novice in business and it is seldom that his training has made him proficient in the discussion

of loans and trade acceptances and stock issues and debentures or of finance and business procedure. He is likely to fit in somewhere between the general manager and the division superintendents. He speaks an unfamiliar language when he explains processes in which hydrolysis and colloidal aggregates and latent heats and reduction curves are involved. He can't get appropriations for research because he isn't understood; he can't make the directors see with his eyes.

Now in just such an establishment in Germany the managing director, a good part of the "Verwaltungsrat," and nearly all the superintendents would be chemists or engineers with good chemical training. Men in administration—on the Verwaltungsrat—understand the problems much better than the American directors. They are as keenly interested in curves as they are in flow-sheets. They are familiar with that greatest of all sporting fields, the field of catalysis, and when the chief chemist who invariably sits in council, tells his fellow directors that Drs. Kleinschmidt and Heisterhagen of their research staff have discovered a new catalyst for the production of one of their wares out of cheaper material, and that they use titanium dioxide, they know immediately that it is available, and the first questions they ask are about the yield, temperatures and pressures required, whether the titanium dioxide gets poisoned, and how it is regenerated. Then, too, they know as well as the chemist how much it is likely to cost to test the process out on a semicommercial scale, and they proceed to get busy. That is the way they keep ahead of the game: by a control organization that understands.

The imaginary situation would be equally well met by a few American corporations, but not by many of them. The others haven't got around to it yet.

Catalysts at Work

Now let us return more specifically to the subject of catalysis. It is an ancient art, but only recently studied earnestly in physical science. There are great tomes written on the subject, and a prevalent theory is that the catalyst is an accelerator; that the reaction is one already taking place, but very slowly, and that the catalyst merely speeds up the reaction. Some men of eminent scholarship oppose the theory; but we have no occasion to discuss the subject in this chapter.

The Manufacture of Sulfuric Acid

The old process requires the presence of nitrous oxides in sulfuric acid chambers to oxidize the vapor of burned sulfur or sulfur dioxide to the anhydride of sulfuric acid or sulfur trioxide. Sulfur trioxide combines with water to make sulfuric acid. The nitrous oxides are used over and over again to effect this change. But sulfuric acid is excessively hygroscopic, which means that it will draw water to it out of the air with an intensity that may be compared to The Old Soak's thirst under prohibition *in excelsis*. To get all the water out by heating the chamber acid is almost an impossibility.

When artificial indigo came along, great quantities of fuming sulfuric acid were needed. This is 100 per cent H_2SO_4 with sulfur trioxide dissolved in it. It is also called *oleum* and it *has* acidic power! The problem was to find a catalyst to take the place of the nitrous oxides so that sulfur might be burned to sulfur dioxide, which, on contact with a catalyst and in the presence of air, which contains 20 per cent oxygen, would be changed to sulfur trioxide. Platinum was found to do it com-

pletely, and some kinds of hot iron rust do it in part. So now, by the contact process, sulfur is burned and the fumes are led first with air through hot iron rust and then through a platinum screen from which the sulfur trioxide falls like heavy snow. The platinum, which is very expensive and which will not act save on contact, is first dissolved as platinum chloride, and magnesium carbonate, which is a very porous body, is dipped into it. That covers the great area of surface with a thin film of platinum chloride solution. It is then calcined, whereby the chlorine and the carbonic acid are driven off, leaving the magnesium oxide or magnesia, also very porous, with all its surfaces covered with platinum.

The Hydrogenation of Fats

Another turn in catalysis, which has been in great use for fifteen years or more, is the so-called hydrogenation of fats. All vegetable and animal oils (but not mineral oils) and hard fats, such as lard or tallow, are closely becousined. Both bodies are compounds of organic acids with glycerol, and these oily and fatty acids are very much alike except for the fact that the fatty acids contain more hydrogen. Now we can bubble hydrogen gas through oils until the cows come home and very little if anything will happen. Everything remains as it was. But under proper conditions of temperature and pressure and in the presence of nickel, the hydrogen will somehow find its way into the oily acid molecules and change them to fatty acid molecules, whereupon the oil becomes hard fat. Being a contact process, we need the greatest available surface of nickel, and so we use it in very finely divided

particles, because the smaller the particles are the greater is the exposed surface of a given weight of the substance.

The Fixation of Nitrogen

Bradley and Lovejoy, two Americans, were the first to fix nitrogen from the air on a large scale, and this they achieved by means of the electric arc at Niagara Falls. The yield was not satisfactory at the time because one little final experiment had not been tried, and the financial backers of the enterprise did not understand. So they called the whole thing off; they had wasted enough money already. A Norwegian saw what they were doing, bethought himself of the very simple last step, and the great nitrogen fixation industry established itself in Norway. But this was electrochemistry, and not catalysis.

At about the same time Professor Haber of Germany came along, saw what Bradley and Lovejoy were up to, and he resolved to fix nitrogen, too. The electrochemical product was nitrate of lime. Haber knew they hadn't water power enough in Germany to follow out the established process, so he brought one volume of nitrogen gas and three of hydrogen together, and tried out a series of catalysts. He found the right one, and now the Haber process is the cheapest method we have for fixing nitrogen. The product is ammonia.

Following this came the war, and while there was plenty of ammonia available there was no source of nitric acid in Germany, and nitric acid is the first requisite in making explosives. But Ostwald had already discovered a method, now in large use, of oxidizing ammonia to nitric acid in the presence of a catalyst. And so the war went on.

Synthetic Methanol

Of late American industry has been disturbed by the immense influx of methanol, otherwise called methyl alcohol or wood alcohol. It is a great solvent. The duty on it is considerable, but the German producers do not mind—they pay it and send more. The reason is that they have found a catalyst, said to be zinc oxide, whereby water gas and steam are brought together in the presence of the catalyst, and out comes a great yield of methanol, nearly 100 per cent pure. Water gas is generated by passing steam over very hot coke in a retort. Compare the cost of this with chopping down hardwood, chipping the wood, distilling it, and then refining the product! Competition is impossible. But it takes long, patient and expensive investigation to get results from such simple directions. The right apparatus must be discovered, the temperatures and pressures for maximum yield determined, and the chances are ten to one that the catalyst has ways of its own that are devious. It may work better in the presence of something else besides zinc oxide.

Acetic Acid

Up in Canada, at Shawinigan Falls, they make calcium carbide by electrochemical means: carbon and lime combined by means of tremendous electric energy. Calcium carbide and water produce acetylene. Acetylene brought into contact with a catalyst under right conditions (originally, I believe, they used mercuric oxide, but now they have a cheaper and better medium), becomes acetaldehyde, and acetaldehyde with manganese sulfate as catalyst becomes glacial acetic acid, which comes out of the reaction chamber like soft ice as thick as a man's arm. This again is cheaper

than distilling hardwood and treating the acetate of lime with sulfuric acid and boiling down the remaining acetic acid to proper concentration.

Ethyl alcohol, which, as John Barleycorn, is itself said to be a catalyst of talking and singing and all kinds of devilment, is probably on the way to catalytic birth. So are other things. But such matters are not to be talked of until they are brought out.

Future Possibilities of Catalysis

There's another possibility in the offing, not yet here, but which may come along some day. It is complex, bewildering, and bound to be full of disappointments, but none the less it is sure to come along in time. One of the unsolved riddles of chemistry is the precise constitution of a lump of coal. There are combinations of carbon and hydrogen and oxygen and nitrogen there that go to pieces as soon as we undertake to find out just what they are. Now a German chemist named Bergius has succeeded, principally by means of high pressures, in introducing hydrogen into heavy oils and also into bituminous coal so that the latter takes on the liquid character of a crude petroleum. Suppose then some chemist were to discover a catalytic method of hydrogenating bituminous coal so that it became liquid, and that this method should become economically possible. Please close the book for a few moments at this point and think what such a discovery would mean. Liquid fuel for everything! No more jockeying for position among the nations to secure their petroleum supplies. No more stoking, no more smoke or cinders, no more worry about the waning supply of petroleum. And no more coal bins.

Chemistry hasn't more than begun to do its proper work for the people yet.

Catalysis, we repeat, is the sporty end of chemistry. The reasons why are not clear, the theories are not developed, and, because we know so little of the subject as yet, procedure goes principally by way of trial and error. Sometimes discoveries are made by accident. In the Badische Works in Germany when they were working on the synthesis of indigo, they needed phthalic acid as an intermediate material. It was expensive, but they reasoned out that they should be able to obtain it by treating naphthalene (which is the white tar product used for making moth balls) with fuming sulfuric acid or oleum. The theory was all right, there was every known reason why it should work, but all the same it didn't. Neither heat nor pressure nor any other stratagem could be made to bring about the desired result. Of course there was no reason to give up the effort, but it was disheartening to meet failure after failure with every attempt to get that reaction of naphthalene to phthalic acid. One day, while one of these experiments was in process, a laboratory boy was told to take a reading from the thermometer. He was a clumsy lad, and he broke the instrument so that a few drops of the mercury fell into the mass. Straightway something happened. The stuff began to seethe and labor, and within a little while there wasn't any naphthalene left; the container was full of the desired phthalic acid! Mercury proved to be the catalyst.

So we might go on filling page after page with catalytic stories and stories of enzymes, which are organic catalysts that effect remarkable changes in the processes of life. The field is immense, amazing, bewildering, romantic, exciting—and we have uncovered only a tiny little edge of the great pall of the unknown, which spreads over it all.

CHAPTER II

THE CHEMIST'S CONTRIBUTIONS TO AVIATION

C. W. Seibel

Helium Division, Bureau of Mines

We of the twentieth century, thinking back perhaps to December 17, 1903, when the airplane of the Wright Brothers, driven by a 16 horsepower gasoline engine, flew some 850 feet in 59 seconds, are likely to think of aerial transportation as a very recent development. Few realize that the beginnings of this art are lost in antiquity. Certain it is that the early legends and myths are replete with winged figures who had the power to travel great distances through the air in short spaces of time. Who is not familiar with the history of Icarus, who, with his father Daedalus, was flying from Crete, and approached so close to the sun that the wax with which his wings were attached was melted and he fell into the sea which now bears his name?

Early records show that this subject of mechanical flight was given considerable thought by the scientists of the period. In the thirteenth century, Roger Bacon, the reputed inventor of gunpowder, is given credit for describing a hollow metal globe filled with "ethereal" air or "fire" which would float in the atmosphere. Two hundred years later, Leonardo da Vinci, the great artist, who was also a scientist of note, sketched a

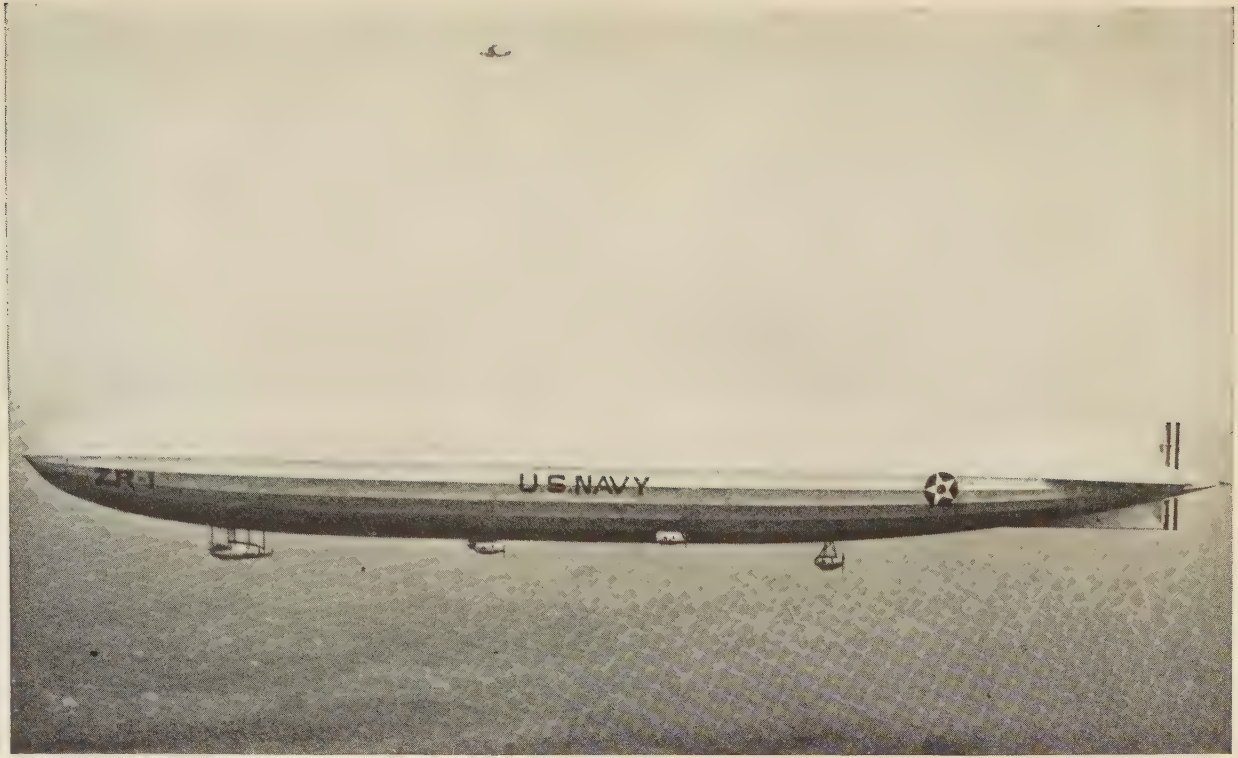
flying machine of the wing-flapping type. Later, in 1670, Francesco Lana, a Jesuit priest, described in detail an airship floated by exhausted metal spheres and provided with paddles to impart motion. This, to some extent, was the forerunner of the modern airship.

Thus, as far back at least as the thirteenth century, man's thoughts on aviation were bent towards two distinct types of machines, the one to be lifted by a buoyant gas, lighter-than-air; the other, an apparatus of the wing type. Likewise today, we have the so-called lighter-than-air and the heavier-than-air craft.

Hydrogen

It was not, however, until some time after the chemist Cavendish had given to the world in 1766 the lightest known substance, hydrogen gas, that man was able to devise means of transporting himself through the air. True, the hot-air balloon of the Montgolfier Brothers was the first to rise, June 5, 1783, but the first cross-country man-carrying flight, in the same year, was made with the aid of hydrogen. Our own Benjamin Franklin happened to be abroad at the time and witnessed the flight. On returning to America, he was asked "What are balloons useful for?" He replied by asking "What is a newly born child useful for?" The development of this infant of 1783 has been closely supervised by its godfather, the chemist, and the present state of the art is, directly or indirectly, largely attributable to his careful guidance and contributions.

Until a few years ago, the most successful of the buoyant gases used for filling the gas cells of an airship was hydrogen. Hydrogen for aeronautical pur-



Official Photograph, U. S. Navy.

A Leviathan and a Pigmy of the Air

poses was undoubtedly first made by the action of acid on some metal, probably iron. This was not an altogether satisfactory method, as one can realize, for to produce 1000 cubic feet of hydrogen, 275 pounds of sulfuric or an equivalent amount of some other acid are required, together with 157 pounds of iron. In order to produce hydrogen for war-time use, the chemist set about to evolve it from substances which could be easily transported and which would be safe to handle—substances which required little apparatus for the actual generation of the gas and which, in turn, could be easily transported from field to field. While undoubtedly General Bonaparte had great difficulty in producing hydrogen for the captive observation balloons which he used in the battle of Fleurus with the Austrians, June 26, 1794, our own soldiers in the late war found it a relatively easy task to make large quantities of hydrogen in small inexpensive plants using the ferrosilicon process, the whole plant being contained on a five-ton truck. It was only necessary to add 58 pounds of a chemical substance called ferrosilicon (a compound of iron and silicon) to 125 pounds of caustic soda which had been dissolved in water, and there was available 1000 cubic feet of quite pure hydrogen. One of the especially desirable features of this method is the fact that the granulated ferrosilicon, a solid substance with a high metallic luster, can be stored without any special precautions as it does not deteriorate in the presence of moisture. The caustic soda is likewise solid and is generally sealed in thin sheet-iron drums, which will stand rough handling. Hydrogen generated by this method costs about $11 per thousand cubic feet, which is perfectly permissible under certain conditions, notably in time of war and where the first cost of the plant must be considered.

For peace times the chemist has devised a means of producing the gas for less than one dollar per thousand, although the plant itself is quite an expensive affair. In this so-called iron contact method retorts are necessary, some of which hold hematite, an iron oxide ore, while others are filled with coke. Steam is passed through the heated coke to form carbon monoxide and hydrogen, which are then passed over the heated iron oxide, reducing it to metallic iron. When this reaction is completed steam alone is passed over the heated iron, whereby the iron is changed back to its original state of iron oxide and hydrogen is freed, the oxygen of the steam having combined with the iron. As will be seen, steam boilers of considerable capacity are needed, which, with the numerous retorts, makes for an expensive installation.

Many other methods of producing hydrogen are available, but the two given and the decomposition of water by an electric current, which is so well recognized that it will not be discussed, are the best known.

Gas Bags

And now having plenty of hydrogen, we must get something to put it in. You have all seen a hot-air balloon ascension at the country fair or at Fourth of July celebrations and have watched the untreated cloth bag slowly ascend with smoke issuing from the seams, from small holes, and from the pores of the cloth itself. Now, if the bag had been filled with hydrogen instead of hot air and smoke, you would have seen nothing at all because hydrogen is a colorless and odorless gas, but it would be leaking out just the same and the balloon would have stayed inflated for only a relatively short period.

DIFFUSION OF GAS THROUGH BALLOON FABRIC

	Weight per square yard, ounces	Diffusion Liters per square meter per 24 hours	
		Hydrogen	Helium
2-ply cotton	12	12	8
3-ply cotton	16	6	4
Single ply, plus gold-beater's skin	4 to 5	0.1 to 1.0	0.1 to 1.0

The problem of finding a satisfactory leak-proof covering was a very difficult one. First, the cloth must be strong and light, for while 1000 cubic feet of hydrogen under operating conditions will lift 68 pounds, it must first lift its containing envelope. Since no cloth as woven is tight enough to prevent the loss of gas, it must be treated in some way to fill up the pores. This filler must not weaken the fabric, must be as strong as possible, waterproof, flexible, not affected by extremes of heat or cold, and withal, light-weight. Many things have been tried, but at present for nonrigid airships (those without a rigid supporting framework) a fabric consisting of two or three plies of long-fiber cotton cloth, cemented together with rubber cement and then vulcanized, seems the most satisfactory. When it is realized that there are over 1500 square yards of surface in one type of airship of 100,000 cubic feet capacity, it will be seen how important it is to reduce the leakage to a minimum. It is of interest to note that it requires more than 27,000 cubic feet of hydrogen to lift the weight of just the envelope of the above ship.

In the case of rigid airships like the Los Angeles and the Shenandoah, the outer covering which you see serves only to streamline the ship and to protect it from the rain. The gas cells, several in number (20 in the Shenandoah) are supported by the structural mem-

bers of the ship. These American gas cells are lightweight cotton cloth with a layer of goldbeater's skin secured to the cloth with rubber cement and then varnished. The German gas cells are also lined with goldbeater's skin, which is impervious to gases, but in this case the skins are secured with a kind of glue. In order to keep the German cells in good condition it is very important that they be kept in a humid atmosphere, while with the American bags this is not so necessary.

In a ship like the Shenandoah, which is 680 feet long and 79 feet in diameter, there are twenty gas cells holding a total of more than two million cubic feet of gas. To line these cells with goldbeater's skin required the skins from over 500,000 animals. This skin is obtained as a membrane from the caecum of the ox, an organ somewhat similar to an appendix, and varies in size, but at the largest may be 18 inches wide by 40 inches long. In addition to its impermeability, it is extremely light and thin.

Obviously, it is very expensive to use cells lined with goldbeater's skin, and it is no wonder that the chemist is hard at work hunting for a substitute. His efforts along this line are beginning to bear fruit and thin sheets made from a substance called viscose show some promise. Viscose is made from wood fiber by treating it first with caustic soda, after which it is aged, treated with carbon disulfide, thoroughly washed, and again aged. Plasticizing materials are added to prevent brittleness, and the product is dissolved in caustic soda, then rolled out in very thin sheets, and fixed in a bath of acid. It is highly transparent and will stand fairly rough treatment. The thin sheets are cemented to the cloth, as is goldbeater's skin, or by another method, a thin coat of the dissolved viscose is spread

on the fabric and the whole is run into the fixing bath and later thoroughly washed. The cost of such cells will be materially less than that of goldbeater's skin, the maintenance of which is at present very expensive.

Viscose, while very impervious to gases in the sheet form, has other important uses. As sheets, it is used for the transparent wrappers of candy boxes; as thin threads, it is our artificial silk.

"Dopes"

The chemist has not confined himself to the treatment of fabrics for lighter-than-air craft, but his skill has been called upon to develop coatings for the cloth coverings of airplane wings and fuselages. In this case it is highly essential that the cloth be held very taut to avoid flapping and loss of speed while flying. So the first problem was to treat the 4½-ounce cotton cloth, which had been mercerized, itself a chemical process, with a substance which would shrink the material in position. A satisfactory substance to perform this duty was found in cellulose nitrate, a substance formed by treating cotton with nitric and sulfuric acids. Cellulose nitrate, itself a solid, would dissolve in ethyl acetate to form a varnish which would shrink the cotton, but the ethyl acetate evaporated too rapidly to make a good job, so its evaporation was retarded by the addition of amyl acetate and denatured alcohol. It was not long, however, until this so-called "dope" began to show a deteriorating effect on the cloth, and in addition it was very inflammable. Though "nitrate" dope has since been fireproofed to a considerable degree, because of its undesirable properties a new dope was sought for. Research developed the new dope from a substance called cellulose acetate.

The manufacture of cellulose acetate is an art in itself, though the process sounds very simple. Just treat cotton with acetic anhydride and acetic acid and dissolve the product in suitable solvents. Unfortunately, unless this treatment and the subsequent aging are carried out under extremely careful chemical control, particularly as regards temperature, the resulting product is insoluble in the desired solvents and therefore useless as a dope. In the manufacture therefore, the temperature is held constant to one degree Centigrade and the closest chemical supervision is maintained. As at first prepared, this dope left a very brittle film on the fabric, so plasticizers are now used to make it more flexible.

Cellulose acetate is much less inflammable than cellulose nitrate and does not injure the coated fabric, but it is not such a good shrinking agent. As a sort of compromise between these two dopes, the wings of airplanes are now given two coats of cellulose acetate dope, then three of cellulose nitrate, and since these are both injured to some extent by sunlight, they are themselves protected by a coat of spar varnish to which a pigment has been added to cut out the injurious light rays. Since there are about two hundred square yards of cloth on the average plane to which are added about 4½ ounces of dope per square yard, about 60 pounds of dope are needed for each plane.

Antiknock Fuels

An interesting development of recent years, and one that is destined to play a very important part in the years to come, is the prevention of detonation (knock) in airplane engines by the use of blended fuels or the addition of certain chemicals to gasoline. Deto-

nation is caused when the gas mixture becomes too hot, either from highly heated carbonized material or from the heat of compression of high compression engines. These high compression engines are very desirable, for they operate on less fuel and give more power than a corresponding engine of lower ratio. By compression ratio is meant the ratio of the volume of the cylinder with the piston at the bottom of the stroke to the volume with the piston at the top. Straight gasoline tends to detonate in these higher compression engines, and so the chemist set about trying to solve the difficulty. It was soon found that alcohol and benzene, for instance, did not detonate so easily. But since the average gasoline has 20,000 B.t.u. (British thermal units) per pound, alcohol 11,500, and benzene 18,000, one can see that it would be necessary to use nearly twice as much alcohol as gasoline, which is clearly out of the question. At present there is insufficient benzene produced to be an important factor when used alone, so blended fuels are used.

It must be remembered in blending engine fuels that the mixture must be volatile enough at low temperatures to permit easy starting and yet not so volatile that it will tend to distill at the high temperatures sometimes attained. One such satisfactory blend consists of alcohol 15 parts, benzene 5 parts, gasoline 80 parts. At first, trouble was encountered in the use of these mixtures because the alcohol always contained water which was thrown out of solution when mixed with gasoline and this tended to catch in the carburetor jets, putting the engine out of commission. This problem of the elimination of water from the alcohol has been solved and the above mixture is finding extensive use. Even in aviation engines of the normal compression ratio type, blended antiknock fuels are

advantageous, since when they are used engines may be operated over a longer period of time before it becomes necessary to take them down for the removal of carbon and general overhauling. That is, a carbonized engine is able to run without detonation using an antiknock fuel where it could not be operated satisfactorily on straight gasoline.

There are other ways of preventing detonation besides the use of blended fuels; one is by the addition of small amounts of certain chemicals, an example of which is tetraethyl lead. This substance is the result of an intensive research by Thomas Midgley, Jr., in the course of which over 2000 different samples of various substances were tried before success crowned his efforts. As an example of its effectiveness, in the short while that it was on the market, the sale had jumped to more than one million gallons of ethylized gas per day.

As first prepared, tetraethyl lead was used in gasoline by itself, but it was soon discovered that the compounds of lead formed by the combustion would fuse with the porcelain of the spark plugs, seriously interfering with their proper functioning. This difficulty was easily remedied, however, by the addition of small amounts of bromine. In decomposing, the lead combined with this element, forming lead bromide, which did not attack the porcelain of the plugs.

Aluminium and Light Alloys

The first power-driven airship, that of the Frenchman, Giffard, contained a three horsepower steam engine which weighed 100 pounds, a marvel of the day. His whole power plant, including the boiler, weighed about 350 pounds, or 117 pounds per horsepower.

Heavier-than-air craft would undoubtedly still be in the experimental stage, had it not been for the advent of the gasoline engine. By the use of this type of engine and the chemist's contribution of aluminium and the light alloys, it is now possible to produce a power plant weighing the same as Giffard's steam engine unit, but developing 200 horsepower instead of three. Thus the weight has been reduced from 117 pounds to 1.75 pounds per horsepower. This great reduction in weight, aside from the design of the equipment itself, is due largely to the use of aluminium castings and alloys in place of iron parts which would weigh approximately three times as much.

In 1855, this metallic element, aluminium, which makes up 7.3 per cent of the earth's crust and which has done so much to make aviation a commercial possibility, was almost a curiosity, costing more than one hundred dollars a pound. The chemist has been able to reduce this to its present value of about 30 cents a pound.

Aluminium is made from an ore called bauxite, found in large quantities in some of the southern states. Bauxite is a clay-like substance consisting of aluminium oxide with the oxides of silica and iron. Since metallic aluminium cannot itself be readily purified, its ore is first treated to remove the foreign elements and leave an almost pure aluminium oxide. Now since the metal is easily oxidized when in the molten condition, the metallurgical process consists of the joint fusion, by means of an electrical current, of the ore with a salt called cryolite, which is a mixture of aluminium and sodium fluoride. In the molten mixture the metallic aluminium is produced at the cathode, generally the floor of the containing vat itself. The fused salt thus protects the molten aluminium

at the bottom of the vat from oxidation until it can be tapped out and run into molds.

Large airships of the type of the Shenandoah and Los Angeles have a rigid framework of metal, inside of which are the gas bags and outside of which is stretched a cloth covering to protect the ship from rain and to give it a streamline form. It would be out of the question to construct such a framework of steel or any of the heavy metals, but by using some of the light aluminium alloys that the chemist has given us, this becomes decidedly practical. Aluminium itself, while light enough, does not have other necessary properties of strength and rigidity, but by combining with it certain other metals, we can produce a really wonderful substance called "Duralumin," which has the following range of compositions:

	Per cent
Copper	3.5 to 4.5
Magnesium	0.2 to 0.75
Manganese	0.4 to 1.0
Aluminium (min.)	92

The hull structure of both the Navy's rigid airships Los Angeles and Shenandoah is made from this alloy.

PHYSICAL PROPERTIES OF DURALUMIN

			Steel
Weight in pounds per cubic feet		173-176	480
Specific gravity		2.80-2.85	7.8
Nonmagnetic			
	Heat-treated	Annealed	Hard-rolled
Tensile strength	55,000-62,000	25,000-35,000	67,000-72,000
Yield point	30,000-36,000	.....	55,000-65,000
Hardness, Brinnell	93-100	54-60	130-140
	Per cent	Per cent	Per cent
Elongation in 2 inches	18-25	10-14	3-8

Duralumin has about the same tensile strength as mild steel. To obtain its maximum strength, however,

it must be heated to a carefully controlled predetermined temperature and quenched. Immediately after this treatment it is quite soft and can be easily formed to desired shapes. The physical properties gradually change over a period of eight to ten days, when it takes on its maximum strength, becoming too brittle for much working. By slightly different heat treatment, however, it can be made to remain in its softened condition indefinitely. These properties lend themselves admirably to fabrication of parts for airplanes and airships.

Alloys of aluminium are not the only ones that have been taken up and used in the construction of aircraft parts. The recent developments in airplane engines, whereby the test period under full throttle has been increased from 50 to over 300 hours, was made possible by the use of alloy steels and other alloys invented by the chemist. These alloys have been responsible for a reduction in weight without sacrifice of strength and have otherwise made for a more efficient engine. As a specific example, one of the most troublesome parts of engines in the past was the valves; these, under the terrific heat of the gases surrounding them, would oxidize, warp, and actually burn up. This would sometimes happen in the first 25 hours of operation, and, of course, an engine is only as good as its valves. By using for these valves an alloy made of iron, silicon, and chromium, the oxidation and warping were greatly reduced, which in itself helped to make the 300-hour test period possible.

Luminous Paints

On the instrument board of the average airplane is mounted an array of dials which serve as indicators

to the pilot telling him at a glance how high he is, what the speed of the engine is, how much gasoline and oil he has, the temperature of the water in the radiator, the direction of flight, etc. Without these indicators flying at night or through fog would have increased danger. The figures and hands of these instruments are made visible at night by means of two chemicals—radium or an equivalent, and zinc sulfide.

Radium and radioactive substances disintegrate steadily and give off alpha rays as one of the decomposition products. These alpha rays are small positively charged particles which, if allowed to strike a properly prepared zinc sulfide screen, cause it to become luminous. At first in the preparation of this luminous paint, some radium salt was used to give the alpha ray. The one-half life period of radium is about 1700 years, which means that at the end of that period the radium would still have one-half of its original activity. Of course, an instrument would in all probability never be used 1/100 of that time even if the zinc sulfide would remain active, and it would probably be burned up by the tiny bombardments before that. For the sake of economy, therefore, a substitute for radium, known as "mesothorium," is now generally used. This substance gives off the necessary alpha rays and for the first three years gives increasing luminosity and then drops off at about one-half for every 7.9 years. The cost of the radioactive material used in this paint on the average watch is about 15 cents. The prepared zinc sulfide and radium salt or its equivalent are carefully mixed by the aid of certain glues, formed into a paste, and applied to the instrument. The luminosity depends to some extent on the technic of mixing the ingredients and upon their application, as well as the activity of the separate

constituents. One interesting thing discovered in the development of this paint is the fact that very pure zinc sulfides do not become luminous under the effects of the alpha ray. It was found after careful research that properly added minute amounts of manganese would produce a satisfactory product. And thus the aviator is assured of being able to see his instruments in the dark as well as in the light.

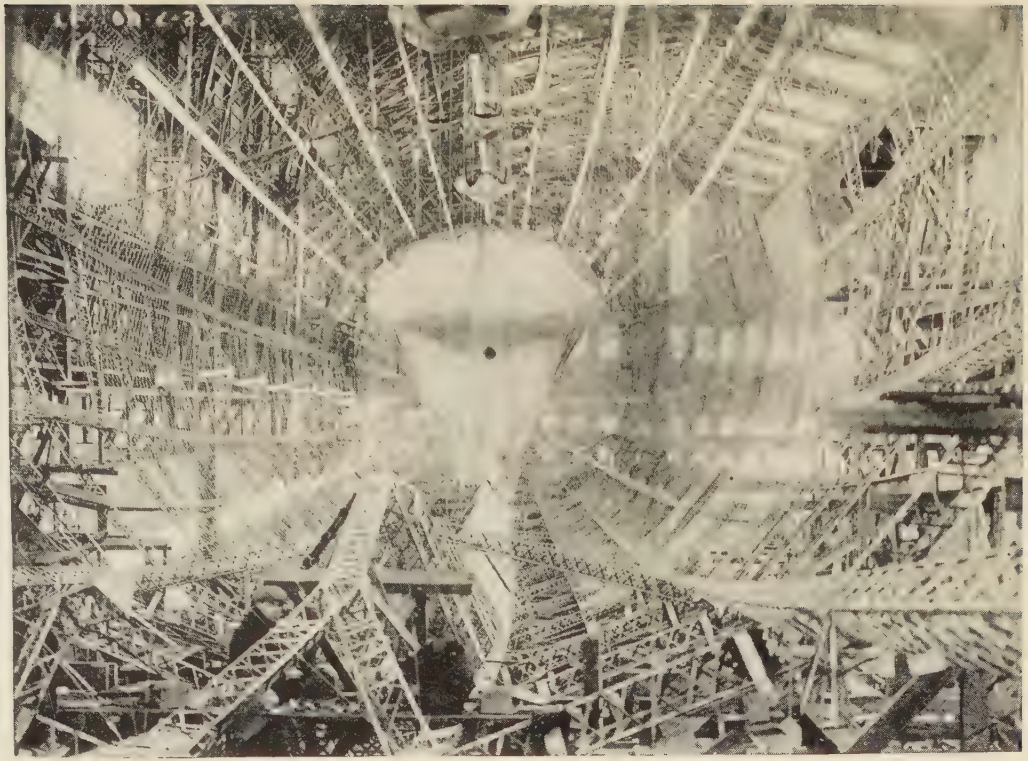
Glues

Glues play a very important part in the fabrication of propellers and the wooden structures of airplanes and airships, and since the life of the aviator depends on their ability to hold two pieces of wood together, with the development of the art of flying has come the development of new glues. Every one knows milk as a food, but few realize that the chemist has made from this common beverage a glue which will hold two pieces of wood together and make them almost as strong as one, and withal, a glue which resists the action of water to a marked degree. By removing all the fat from milk and then allowing it to sour, a curd is formed which the scientist calls casein. This substance washed, dried and ground, comprises the base of the so-called casein glues. Other substances usually added are lime, silicate of soda, and water. There are several types of such glues, depending upon the percentage of the various ingredients added, but when properly compounded and used, the glued product is almost as strong as if hide glue, the strongest of glues, had been used. Hide glue, however, is not very water-resistant, while wood glued with a casein preparation will show no separation of plies after boiling in water for eight hours.

A more water-resistant glue than this, however, has been developed, though it is not quite so strong. Blood albumin glue, as the name implies, is made from fresh blood, processing it to remove the fibrin and part of the red corpuscles and then evaporating to dryness. When this dried blood is dissolved in water and small amounts of ammonia and lime are added, a glue results which, although the glued parts must be baked under pressure at 160° F., has wonderful water-resisting properties, showing from 50 to 75 per cent of its dry shearing strength after soaking or boiling for relatively long periods. Blood albumin glue is used principally for ply wood because it can be applied so as not to stain through the thinnest veneer and because of its waterproof qualities. Ply wood enters largely into the construction of airplane parts.

Helium

At the outbreak of the World War, the Zeppelin Company had constructed more than thirty airships, somewhat less than half of which were in a serviceable condition. They were at once put into military service with such success that the Allies immediately began to look around for their equal or superior. For scouting purposes with the fleet, the statement has been made that one hydrogen-filled dirigible, under certain conditions, could render service equal to that of six scout cruisers. This statement was made notwithstanding the fact that there has always been some danger accompanying the use of hydrogen-inflated craft, due to the fact that this gas is very inflammable. Also, air diffuses into the gas envelope in the course of time and may form an explosive mixture with the hydrogen. In addition,



Official Photograph, U. S. Navy.

One of the Partly Inflated Gas Cells in the Duralumin Hull of the Airship Shenandoah.
Note the size of man at left.

it had been clearly shown that incendiary bullets could bring down the largest hydrogen-filled Zeppelin a mass of flames. The English soon realized that a noninflammable balloon gas would be a tremendous advantage, for nothing short of a direct hit with a relatively large caliber gun would have any immediate effect. The only noninflammable, nonexplosive gas which would have the required lifting force was the rare gas, helium. Helium was known to exist in the atmosphere of the sun long before it was discovered on the earth by Sir William Ramsay in 1895, in the gas given off from a heated mineral, cleveite. Shortly thereafter, its physical properties were worked out showing it to be absolutely inert, liquefying at –268° C., and having 92 per cent of the lifting value of hydrogen.

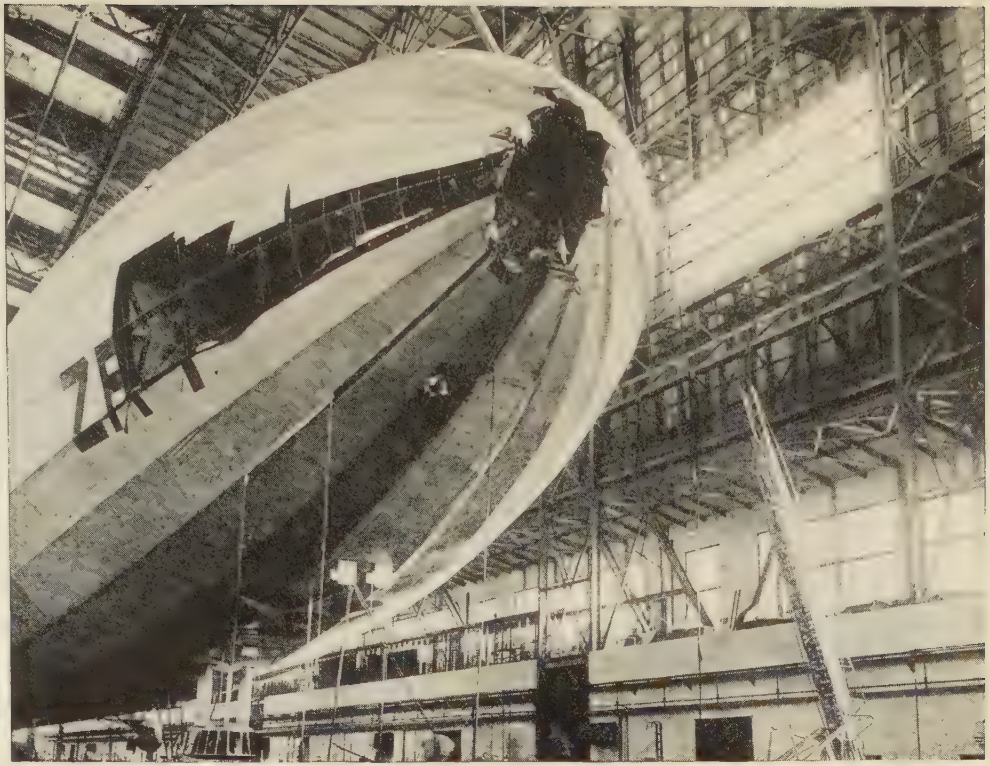
The English knew that Dr. H. P. Cady and David McFarland had discovered as much as 2 per cent of helium in natural gas from certain fields in Kansas. After the entry of the United States into the World War, they suggested that we look into the possibility of the production of helium from natural gas for balloon purposes, stating that they would be willing to pay as much as one dollar a cubic foot for it. This is approximately one hundred times the cost of hydrogen. At this time there were not twenty-five cubic feet of helium in existence and the price when purchasable was $2500 per cubic foot. The smallest useful balloon holds about 17,000 cubic feet.

After a hurried field survey, it was decided that the natural gas from the Petrolia field of Texas offered the best possibility. All the helium so far commercially produced has come from this field. Natural gas from the Petrolia field has the following composition:

	Per cent
Helium	0.94
Carbon dioxide	0.25
Methane	56.85
Ethane	10.33
Nitrogen	31.63

At the start of this problem the chemist knew that helium could not be liquefied by any ordinary means. On the other hand, it was known that under normal pressure, methane or marsh gas would liquefy at –164° C., ethane at –93° C., while nitrogen required a temperature of –196° C. to convert it into a liquid.

Details of the process of helium production are still considered in the nature of military secrets, but in general they consist of the production of a sufficiently low temperature to liquefy all the constituents of natural gas except helium. This low temperature can be produced in a manner similar to that used in the production of liquid air, using in place of air either the natural gas itself or nitrogen. Air is not used because liquid oxygen from the air might come in contact and mix with liquid methane from the natural gas, forming a mixture as dangerous as nitroglycerine. So either nitrogen or natural gas or sometimes both, though in separate cycles, are compressed, in some cases to as high as three thousand pounds per square inch, the heat of compression is removed by proper means, and the compressed gas is sent through heat interchangers, which may consist of one tube inside another. The incoming gas is sent, say, through the inside tube and after traveling its length is allowed to expand, thereby materially lowering its temperature. This cooled gas is then sent back through the annular space between the two concentric tubes, cool-



Official Photograph, U. S. Navy.

Torn from its mooring mast in a 75-mile gale, the helium-filled Shenandoah returned to the hangar under its own power. Inflated with hydrogen, the story might have been different.

ing the incoming gas somewhat. This progressively keeps up until a temperature is reached which, with the pressure used, will liquefy all the constituents except the helium. It is, of course, relatively easy to remove the gaseous helium from the liquid. The helium, 94 per cent pure, is compressed into bottles at 2000 pounds pressure for shipment. The liquefied gas is vaporized in such a way as to make use of its low temperature and returned to the pipe line for domestic consumption.

At the time of the signing of the Armistice, a little more than a year after the project was started, there were on the dock at New Orleans, bound for France, 250,000 cubic feet of 92 per cent helium, which had been produced for less than 45 cents per cubic foot. There is now being operated at Ft. Worth, Texas, a plant producing nearly one million cubic feet of helium per month. This is a plant designed and operated by the Linde Air Products Company under government supervision. Another plant is in the process of erection, having been designed by government engineers from the results of government researches on the subject.

When it is considered that the gas being processed contains less than one per cent of the desired element and that numerous problems such as the removal of water vapor and carbon dioxide, the production of nitrogen from the gas for use as a refrigeration medium, the effect of temperature and pressure on the solubility of helium in the liquefied portions of the natural gas, and many others had to be solved, and that every day more than five million cubic feet of gas must be cooled to considerably more than 100 degrees below zero Centigrade, it is remarkable that

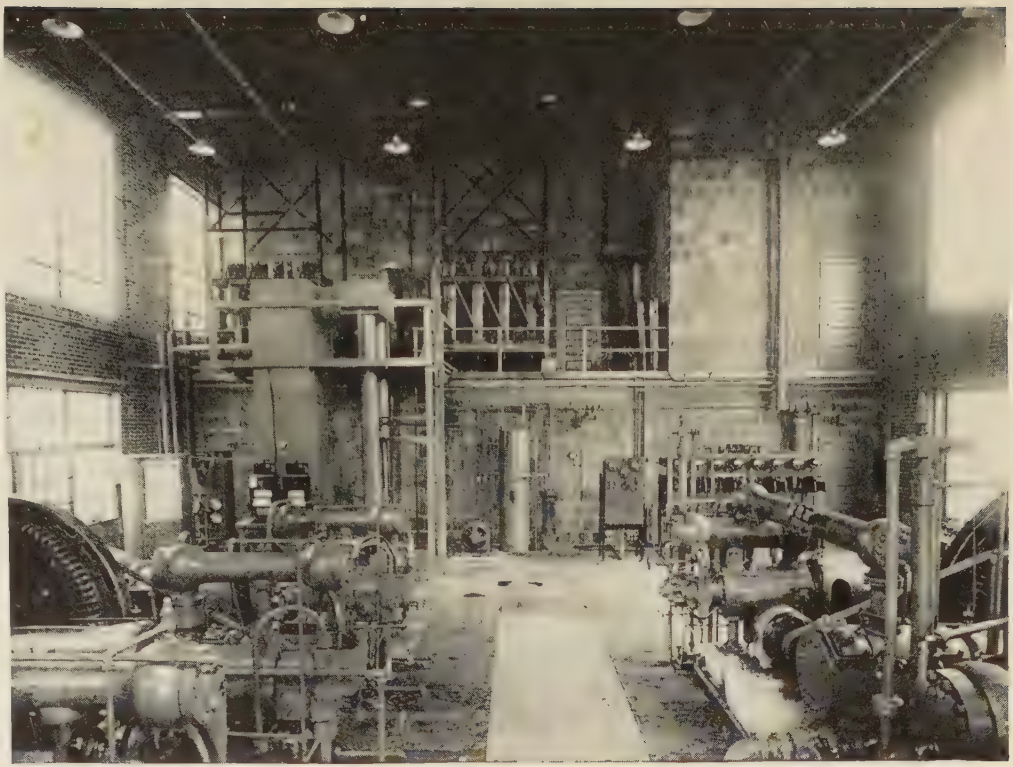
this much desired balloon gas, once so rare, is now being produced for $30 per thousand cubic feet.

The relative cost of hydrogen and helium for airship operation seems to be slightly in favor of helium, provided yearly cost is considered. As has been mentioned, air always diffuses into the gas envelope, whether hydrogen or helium be used. In the case of hydrogen, when its purity has dropped to 85 per cent, sometimes even 90 per cent, the envelope must be deflated because of fire risk and danger of explosion. It is not considered safe to try to purify this hydrogen, so it is allowed to escape to the atmosphere. The ship must then be inflated with pure gas. This operation is necessary eight to ten times a year.

When air diffuses into a helium-filled ship, the only serious effect is to decrease the lifting power. In this case, however, the helium can be purified at about $1.50 a thousand. So with hydrogen at $11 per thousand and helium at $30, the yearly cost is slightly less when helium is used.

The purification of helium is carried out in a plant developed by the Bureau of Mines, the writer having had charge of the project. This process is somewhat similar to that already described for the production of helium, but since there is now no methane in the gas, the refrigerating cycle employs air instead of nitrogen. The helium is compressed to two thousand pounds per square inch and then cooled to the temperature of liquid air, and the liquid is separated from the gaseous helium as in the production process. The highest purity yet produced commercially is obtained from this plant, namely 98 per cent.

And so we see that in this, as well as other industries, the chemist has been making possible the impossible.



Official Photograph, U. S. Navy.

Helium Purification Plant Built by the Bureau of Mines for the U. S. Naval Air Station, Lakehurst, N. J.

Future Work

It is only necessary to think back to the years 1910-14 during which time the German airship companies carried a total of over 17,000 passengers a distance of over 100,000 miles without fatality to bring home the possibilities of aerial transportation. With it will come more efficient equipment. There is still much work to be done along all of the various phases mentioned above. To the one who can incorporate small quantities of hydrogen in our present gasoline and keep it in solution will go the fruits attending the use of an excellent antiknock. Every ounce of weight is begrudged by the airplane manufacturer and he would pay high prices for a lighter dope which would accomplish the purpose. Blended fuels or synthetic ones offer an interesting field of research. The alloy metals have startling possibilities and a more impervious gas envelope to contain hydrogen and helium is to be desired.

Reading References

Grard. Aluminum. D. Van Nostrand Co., New York.

Pratt, H. B. Commercial Airships. Thos. Nelson & Sons, London.

Vivian, E. C., and March, W. Lockwood. A History of Aeronautics. W. Collins & Sons, London.

Government Publications:

National Advisory Committee for Aeronautics. Report No. 66, Glue Used in Airplane Parts; Report No. 33, 1918, page 339, Self-Luminous Material; 1918, page 410, Airplane Dopes and Doping.

Aviation Fuel—Grade A. Technical Note 134. Navy Department.

Helium-bearing Natural Gas. G. Sherburne Rogers. Technical Paper 121, U. S. Geological Survey.

Properties and Treatment of Duralumin. Technical Note 136. Navy Department.

Journal Articles:

Cady, H. P., and McFarland, David. Helium in Natural Gas. Journal of the American Chemical Society, Vol. 29, 1907, page 1522.

Chandler, Lt. Col. C. deF. Hydrogen for Military Purposes. Aerial Age, 1917.

Sparrow, Stanwood W. Fuel Requirements of Internal Combustion Engines. Industrial and Engineering Chemistry, Vol. 15, 1923, page 476.

Wilson, L. P. Artificial Silk. Journal of the Society of Chemical Industry, 1917, page 817.

Worden, E. C. Cellulose Acetate. Journal of the Society of Chemical Industry, 1919, page 370.

CHAPTER III

CASEIN
A WASTE OF ONE INDUSTRY MADE THE RAW MATERIAL OF MANY OTHERS

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The study of casein and its application to industry holds out very interesting possibilities to the research chemist. In the first place we know very little about the chemistry of casein, all present methods of preparation and utilization being based upon a few reactions which are themselves very imperfectly understood. The literature on the subject is very meager and, particularly in the case of the patent literature, misleading or actually inaccurate. In the second place, there is a tremendous amount of skim milk going to waste in this country. The demand for cream has caused the production of milk to increase to such proportions that the recovery of the by-products and their utilization has become a very important matter.

The Casein Industry

Cheese has been known and used by man as a foodstuff as far back as we have authentic records. It was obtained by permitting or causing the milk to sour, which caused a white solid mass or curd to form. This mass consisted of casein, together with butter

fat and some albumin. The curd so formed was separated from the watery residue, or whey, pressed into more or less compact masses, and aged or further treated to produce the flavor and consistency desired.

This was the beginning of the casein industry. Comparatively little progress was made, aside from improvements in cheese and methods for producing it, until recent years. With the progress of civilization and the conversion of the luxuries of yesterday into the necessities of today, increased demands for butter fat to be used in the manufacture of butter and ice cream created the great creameries. These creameries, particularly in this country where rapid growth has compelled a disregard for waste, extracted the butter fat or cream from the milk and wasted the remainder, frequently at the expense of good sanitary conditions in the district.

To appreciate the magnitude of this waste, consider for a moment an average analysis of cow's milk. (Only cow's milk will be considered in this chapter, as this is the source of practically all commercial caseins at present.)

	Per cent
Water	87.27
Fat	3.64
Casein	3.02
Milk Sugar	4.88
Albumin	.53
Ash (Inorganic Salts)	.71

Until recently, only the fat was utilized, yet there is nearly as much casein and over one per cent more milk sugar than fat. To recover these by-products economically and find industrial use for them has been and is the problem of the industrial chemist. Considerable progress has been made in this line (largely

in the laboratories and plants of industrial organizations which do not publish their findings), but there remains much yet to be done. There is at the present time an estimated quantity of 22,500,000,000 pounds of skim milk annually available in the United States. Skim milk is milk from which the cream or butter fat has been removed. Government reports for 1923 show that in that year 14,500,000 pounds of casein were produced—4,745,000 pounds in California, 3,060,000 pounds in Wisconsin, 2,490,000 pounds in New York, and the balance scattered through a number of other states. The same report shows a total production of but 2,872,000 pounds of milk sugar, of which 884,000 pounds were produced in California, none in Wisconsin, and 916,000 in New York. The problem will remain but partially solved until all available casein, milk sugar, and albumin are recovered and put to good productive uses.

The Production of Casein

Casein is the name applied to a group of related compounds found in milk, which in general react as a unit and have similar properties. The exact structural composition of these compounds has not been determined, but some of them, if not all, are known to contain amino groups, so casein is classed as a protein. A typical analysis (there are a number of these to be found in the literature) gives the following:

	Per cent
Carbon	52.69
Hydrogen	6.81
Oxygen	23.14
Nitrogen	15.65
Sulfur	.83
Phosphorus	.88

Results of such analyses show sufficiently close agreement regardless of the source of the casein (whether from cow's milk or from the milk of other mammals), to indicate that there is a very close relationship, tending almost to combination, between these compounds. Of course, very little can be safely deduced from such analyses, as there are a number of other organic compounds with entirely different properties in which practically the same percentage composition is possible. What can definitely be stated is that casein is a colloid which is soluble in dilute alkalies and concentrated acids, and which is coagulated or precipitated from solution by dilute acids. It exists in milk in what might be termed a state of dispersed equilibrium, i.e., neither in solution nor in the aggregate or clotted state, which equilibrium is disturbed by souring of the milk (production of lactic acid), by the addition of a mineral acid or strong organic (acetic) acid, or by the action of an enzyme, such as rennet. Advantage is taken of this property in the commercial production of casein and in consequence there are three principal types or kinds on the market, known as self-soured or lactic casein, acid casein, and rennet casein. These vary in properties and composition, the principal difference being between the acid casein and rennet casein, the self-soured being really an acid-coagulated product.

Self-Soured or Lactic Acid Casein

A larger volume of self-soured casein is used in this country than is produced here at present. The bulk of the imported article comes from Argentina and from France and is of such uniform quality as to give it a very good market, especially in the paper indus-

try. It is prepared by running the skim milk, from which the cream has been carefully separated, into vats, adding a little sour milk or culture of lactic acid bacteria, and allowing souring or fermentation to take place until curdling is complete. The contents of the vat are then slowly heated to around 140° F. and the curd is broken up by agitation. The clear whey is run off, the curd is washed with several successive portions of clean water, then transferred to a moderate pressure press, such as a cheese press, and excess water is expelled. The resulting cakes are broken up and spread in thin layers on canvas-covered trays to dry. The drying may be effected in the air or more rapidly in a steam-heated drying room, the trays in this case being piled up on a wheeled truck with space for air circulation between them. The dried casein is granular, horn-like, and ranges in color from straw to buff, depending upon its degree of purity. Control of the drying temperature, where steam drying is used, has a very important effect upon the color of the casein. If too high, the color deepens from yellowish to almost orange, the discoloration taking place the more readily if the casein is contaminated with traces of milk sugar, which should have been removed when the curd was washed.

A considerable amount of the domestic self-soured casein is made by small operators, who do not follow a carefully controlled method of manufacture, and whose product is far from uniform in quality. The skim milk is allowed to sour in vats or tubs. When coagulation is complete, the curd is broken up with wooden rakes, while the whole is heated to 135° to 165° F. This causes ready separation of the whey, which is then drawn off and used as hog food. The curd is placed in bags and pressed to remove excess

liquid, then broken up and dried on trays. Some operators wash the curd twice with water, some once, and many do not wash it at all. Lack of uniformity is inevitable.

Acid Caseins

Acid caseins are commercially designated by the name of the acid used in their preparation. In this country the most important are sulfuric and muriatic (hydrochloric). Acid coagulation requires less time than the self-soured process and lends itself more readily to close chemical control; hence the product should be more uniform, although this is not always the case. The major part of acid caseins on the market are of domestic manufacture.

The milk is centrifuged to remove the maximum butter fat as cream, for which there is always a good market. The skim milk is treated, in vats equipped with agitators and either an open or closed steam coil, with the proper amount of very dilute acid to produce complete coagulation. During the addition of the acid the milk is kept agitated in order to diffuse the acid solution quickly and uniformly and so prevent the formation of the curd in large clots or strings. When coagulation is complete—as may be determined by drawing off a test glass of the clear whey and adding a few drops of acid to it—the contents of the vat are heated by means of the steam coil to about 140° F. The agitators are then stopped, the curd is allowed to settle, and the major part of the whey is siphoned or pumped off into another tank for treatment to recover milk sugar if muriatic (hydrochloric) acid was the coagulant, or wasted if sulfuric was used. The curd is agitated with several successive portions of clean water, then the whole contents of the vat are dropped

into the basket of a centrifugal wringer or pumped through a filter press. The semidry caked curd is broken up and dried on canvas-covered trays, racked as described above, in a steam-heated drier. The product resembles self-soured casein in appearance and in general characteristics, though the color is frequently somewhat lighter and the taste and odor are sweeter.

Unfortunately, as in the case of the self-soured casein, all the acid caseins found on the market at present are not made by such a carefully controlled process, and in consequence, there is a lack of uniformity in the product. The old, so-called wet curd process is rapidly being replaced by the more modern process just described; so within a few years the average quality of acid caseins will doubtless materially improve.

The wet curd process is used where it is not convenient or economical to ship the milk, as such, to the large creamery or casein plant. Small creameries or the farmers themselves separate the cream and ship that, then treat the skim milk with acid according to directions. The curd is drained, sometimes washed, pressed into barrels, and so shipped. When it arrives at the casein plant, the contents of the barrels are dumped into vats, and the curd is broken up, washed with water, and dried as described above. Sometimes the curd is dissolved in alkali and reprecipitated with acid, which treatment gives, in general, a better quality casein, but also materially increases the costs, and so is not in general use.

Several days may elapse between the time the curd is formed and its arrival at the casein plant, and frequently there is more or less decomposition of the casein through bacterial action. The small operators seldom perfectly wash the curd, if at all, so the soluble

impurities have opportunity to become adsorbed to such an extent that their complete removal by washing would be difficult. Any fat not removed by the cream separator is largely carried down with the casein upon coagulation. As the types and methods of operating separators on a small scale vary, so will the fat content in the casein vary. The writer has found from 0.5 to 1.8 per cent fat in commercial domestic acid caseins, the last being a wet curd process casein.

Rennet Casein

In the manufacture of rennet casein only fresh skim milk separated as completely as possible from butter fat can be used. To the milk, heated to about 104° F., is added the rennet solution containing about one part rennet to five thousand parts of milk. Rennet is an enzyme obtained from the lining of calves' stomachs and is sold on the market in the form of a dry powder or a very concentrated solution. During and after the addition of the rennet, the milk should be constantly and uniformly agitated until coagulation takes place, a matter of fifteen or twenty minutes. Coagulation with rennet is not coincident with the addition of the coagulant, as in the acid process, but if the solution is not kept gently agitated, the coagulation will take place en masse, giving a curd which is very difficult to break up for proper separation of the whey. When the coagulation is complete, agitation should be stopped, the curd allowed to settle, and the whey drawn off as described above. This whey contains milk sugar and albumin, the first in excellent condition for recovery, since in the practically neutral solution there is no chance for inversion as in acid coagulations. The curd is washed first with

water at about 170° F., then with cold water, centrifuged or filtered, and dried on trays as described above.

Properly controlled, this method gives a high quality product which is used in edible caseins and in the manufacture of casein plastics. It has a peculiarly characteristic granular structure, its color varies from cream to almost pure white, and it has a faint sweet milky odor and no taste. Good quality rennet casein is manufactured in France, Australia, and New Zealand. These average lower in fat content than the other caseins, probably because of improved methods or greater care in the separation of the cream. The writer has found as low as 0.07 per cent fat in a good French rennet casein. There has been no large outlet for rennet casein in this country until recently, hence practically none was produced. With the inception of the casein plastics industry here, production of rennet casein was started and it is quite safe to predict that these two industries will develop side by side.

The manufacture of casein is likely to be rather seasonable. During the spring and summer months there is normally greater production of milk than can be used for food as such, while during the winter months the balance is apt to be in the other direction. Casein would naturally be largely manufactured during the flush period and the dry product stored to tide over the winter demand. It is here that the Argentine and Australian products can work in to advantage, as their summer comes at the time of our winter.

Properties of Casein

There is a very marked difference between the acid caseins and rennet casein. As mentioned before, casein, so far as is now known, is not a definite chemi-

cal individual, but a group of related compounds, colloidal in nature. In milk there exists some sort of combination or close relationship between the casein and certain inorganic substances, principally lime and phosphoric acid. When casein is coagulated with acid, this combination seems to be broken up, the lime remaining in solution together with the major part of the phosphoric acid.

Acid caseins hold a certain amount of adsorber or occluded acid and consequently neutral distilled water percolated through finely ground acid casein will give an acid reaction towards indicators, such as litmus. There is a strong probability that the organic compounds which go to make up acid caseins are themselves acids, but the writer has seen no positive proof of this. The major part of commercial acid caseins is insoluble in water.

Acid caseins are all soluble in dilute alkalies, ammonia, and alkaline earths and are reprecipitated from such solutions by dilute acids. They are also soluble in concentrated acids, such as 37 per cent hydrochloric and glacial acetic, from which solutions they are reprecipitated by the addition of water. A 2 per cent aqueous ammonia solution at 70° C. readily dissolves enough acid casein to give about a 10 per cent solution. If formaldehyde in excess, but diluted with water, be added to this solution while it is well agitated, after a few minutes the whole coagulates en masse to a white jelly-like substance. If this is allowed to stand, the jelly gradually becomes tough and sponge-like and clear liquid can be expelled by applying pressure. This tough, spongy material does not redissolve in dilute alkalies, but is converted by them into a transparent jelly.

The conditions attending the coagulation of casein

by the action of rennet are quite different from those where acid is used. The milk must be sweet and the rennet itself is neutral in reaction. If acid is present in any appreciable amount, the purity of the product is of necessity impaired. A good rennet casein will have an ash of about 7.5 per cent which analysis shows is chiefly lime and phosphoric acid. Hence it is evident that the combination of casein with these substances in the milk is not broken up by rennet coagulation, as it is by acid, but rather more firmly established. In fact, rennet casein is frequently designated calcium caseinate, a loose term in itself, but indicating the fact that in rennet casein there is some sort of combination with lime whereas in acid caseins there is none. Rennet casein contains no occluded acid and, so far as the writer has been able to determine, possesses neither acidic nor basic properties.

Rennet casein dissolves in alkalies much less readily than acid caseins, a 2 per cent aqueous ammonia solution producing at best and more slowly a 7 per cent casein solution with rennet casein. From an alkaline solution of rennet casein acids will precipitate acid caseins, but rennet will not reprecipitate rennet casein. From an ammoniacal solution, formaldehyde will cause the formation of a white jelly-like substance somewhat less readily than from ammoniacal solutions of acid caseins. This substance becomes less tough and sponge-like than that described above and in consequence gives up the entrapped liquid less readily. It is also insoluble in alkalies, indicating that the formaldehyde has in some manner changed the casein.

This action of formaldehyde on casein, either acid or rennet, is imperfectly understood, but it is of considerable commercial importance and has great industrial possibilities. Upon this reaction is based the

casein plastics industry, as will be shown later. To alkaline solutions of casein a small amount of formaldehyde may be added without causing coagulation. If this solution is spread in thin films on wood, paper, brick-work, etc., upon drying a hardened coat of casein will be left, which will be tougher and more moisture-resistant than the unhardened. Solutions of bichromates, tannin, and acetone as well as other aldehydes, such as acetaldehyde and furfural, produce effects somewhat analogous to that of formaldehyde, but at the present time none of these are of industrial importance. Considerable research can advantageously be done along this line, as without doubt numerous applications could be made of this reaction if it were carefully studied.

Industrial Applications

Some of the most important present-day industrial applications of casein will now be briefly considered. Further study of casein and its reactions, both those now known and others not yet discovered, will quite probably in a few years materially increase the number of industries which can apply it to advantage, but now it is used in the preparation of coating for paper, for glue, for cold-water paints, in the printing of wall paper and fabrics, and in the manufacture of plastic material, which replaces horn, celluloid, hard rubber, etc., in the trades.

Paper Coating

Before it was discovered that casein could be used as a binder for the pigment in mixtures for coating paper, animal glue was largely used for this purpose. The

Courtesy, Martin Cantine Company.

Paper-Coating Machines.

coating containing glue was much more affected by moisture than that containing casein; it expanded appreciably with absorption of moisture and contracted a like amount upon the evaporation of the moisture. Because of this property, it was necessary to use great care in printing polychrome effects; otherwise the colors did not strike where intended. Coatings containing casein do not possess to any serious extent this objectionable property and they take the ink so sharply that wonderful detail effects are possible with them.

The process for coating paper is quite simple to outline, but, like many other processes dependent upon substances colloidal in nature, is sometimes rather complicated in operation. Its success is largely dependent upon the preparation and use of a casein solution of the proper viscosity. This solution is usually made with casein, borax, and water with a small amount of ammonia, the last producing a somewhat more moisture-resistant coating upon drying than if omitted. Powdered China clay, satin white, or other white pigment, is added in proper amount and the whole very thoroughly stirred to produce a perfectly smooth or homogeneous mixture. This is applied to the paper in a smooth, even coat by means of a special machine, fitted with rolls which are automatically fed with the coating mixture. The paper is run through a steam-heated drier, where the temperature is so regulated as to dry the coat rapidly but not discolor it. If a high glossy finish is desired, the paper is then put through a series of calender rolls; if a satin, egg-shell finish, the process is complete with the drying. The paper is made up into rolls and is ready for the market.

If the casein solution is too viscous, it is very difficult to produce with it a perfectly smooth, even coat. Also, when stirring in the China clay or satin white, it

will become filled with small air bubbles, which are very difficult to remove and if not removed, produce pin holes in the coat. These are very objectionable, and in fact, spoil the paper for its intended uses. If the casein solution is not viscous enough, it does not properly hold the pigment in suspension, thus causing streaking and lack of uniformity in the coat. Self-soured, sulfuric and muriatic caseins are used in this industry. In general, self-soured casein produces solutions of the lowest viscosity and muriatic casein of the highest, so care must be exercised to apply the proper formula to the right casein.

Casein Glue

It has long been known that a mixture of casein and lime water produces a glue or cement which is not only as strong but more water-resistant than animal glues. This glue, however, sets rather quickly (the more rapidly the higher the percentage of lime) and after setting is worthless, so it has not been popular. Within recent years it has been discovered that the presence of a very small amount of sodium fluoride, copper chloride, or other chemical in the mixture not only materially retards the setting, but at the same time increases the water-resistant property of the glue and acts as a preservative. Other modifications and improvements have been made, such, for example, as the addition of sodium silicate, which also reacts with the lime to produce a cement, and of small amounts of oils, such as kerosene, which prevent the dry mixture from caking in the containers. The result is that, as the modern casein glues have become better known and their properties and advantages appreciated, their popularity, especially among wood workers, has steadily increased.

Joints glued with casein glue when properly set are stronger than any of the usual commercial woods themselves and are practically unaffected by moisture. This, in connection with the fact that casein glues are no more expensive than animal glues of equal strength and are much easier to mix and prepare for use, assures this industry a good future.

During the war with Germany, casein glue was found to be the only glue or cement which would successfully stand up under the rigid tests prescribed for a cement for ply wood in airplane construction. In one of these tests the glued piece was boiled in water for over an hour, very extreme treatment, but for such work only materials which would stand up under extreme tests could be considered.

Casein glue is frequently called "cold-water glue," because it must be mixed with cold rather than hot water and is used cold. This is contrary to the procedure with animal glues, which must be prepared with hot water and kept hot while in use. The exact chemical action of sodium fluoride or copper chloride in the lime-casein mixture is not understood; it would without doubt be an interesting study, but not one with apparent industrial value, as the results are well known and applied. Self-soured, sulfuric and muriatic caseins are used in the preparation of casein glues.

Casein Paints

Cold-water paints may consist merely of water and the pigment, as, for example, whitewash, or of water, the pigment, and a binder, such as animal glue or lime-casein mixture which is practically a thin casein glue. The first readily rubs or flakes off. Paint with animal glue binder is not at all water-resistant, and

walls painted with it must not be subjected to moisture and cannot satisfactorily be cleaned by means of a damp cloth. Paints with the lime-casein binder dry with a smooth egg-shell-like coat which is practically water-resistant so far as ordinary interior conditions are concerned and which may be cleaned with water quite satisfactorily. Casein is here put into solution with lime water, which in drying exposed to air absorbs carbon dioxide, forming some kind of calcium carbonate-casein compound. This compound or combination is insoluble in water, hence the water-resistance of the coat. Casein paints are made in various colors, the color being dependent upon the pigment used. In general, they consist of self-soured or acid casein, lime, finely powdered chalk, inert pigment to give the color desired, and water. They are principally used for interior work, though there are some which claim sufficient water-resistance for exterior use.

Besides their application in the strict sense as paints, these mixtures are being used with considerable success as water colors in the printing of wall papers. They are also used in the textile industry in the printing of designs on certain classes of fabrics.

Casein Plastics

The casein plastics industry in this country is in its infancy, but it is sure to develop rapidly, as the product has much to recommend it. This industry is well established in Europe, the original material having been made in Germany by patent processes and sold under the trade name Galalith (Greek for "milk stone"). Since the war and with the expiration of the basic patents, the industry has sprung up in Austria, Hol-

land, England, France, Italy, and the United States.

The first American casein plastic to be manufactured successfully is known by the trade name Karolith. It was developed independent of foreign information or assistance at the Mellon Institute of Industrial Research, Pittsburgh, by two American research chemists, another evidence of the fallacy of the belief in the superiority of European, particularly German, research workers.

Casein plastic material is tough and horn-like, is capable of readily taking and retaining a high polish, and is practically noninflammable, odorless, and tasteless. It can be dyed any color or produced with streaked or mottled effects, rivaling horn, ivory, coral, jade, tortoise shell and the like, for beauty. It tools reasonably easily, can be embossed, and has comparatively high dielectric and tensile strengths. It is at present used largely for high quality buttons, buckles, novelties, beads, fountain pens, automatic pencils, etc., but, as can readily be appreciated, there will develop many other uses for a material which so ideally combines beauty with strength.

There are two principal processes for the manufacture of this material, a wet and a dry process. Practically all patents on the subjects are concerned with modifications of either of these or with attempts to produce a molding compound with casein. Fundamentally, either process depends upon the reaction of formaldehyde or some other hardening agent with casein. In the wet process, a solution of casein in an alkali or ammonia is first prepared. Dyestuffs, pigments, or fillers are stirred in to produce the desired color or effect and the casein is coagulated by the addition of a coagulant, such as an acid. The coagulum is pressed into sheets or rods in hydraulic presses, then

hardened in a formaldehyde bath and seasoned in a drying kiln. This is the older process which is today largely supplanted by the dry process.

As the name indicates, the casein is not put into solution in the dry process, but ground to a fine powder and mixed with dyestuffs, or fillers, and water. It is then put through extruding machines or heated calender rolls, which convert the powder by means of heat and pressure into plastic rods or masses. These masses are pressed into sheets in hydraulic presses and the sheets (or the rods from the extruding machines) placed in a formaldehyde bath to harden. They are seasoned in drying kilns in the same way as material produced by the wet process, but the time required for seasoning is somewhat shorter. Rennet casein gives the best results with the dry process and so is very largely used in the casein plastics industry. Material manufactured from acid caseins is, in general, more brittle and less uniform in color.

Miscellaneous Industrial Applications

Rennet or self-soured casein of a high degree of purity finds some application in the preparation of special foods. The casein is mixed dry and finely powdered with a solvent, such as borax, sodium bicarbonate, or sodium glycolate, which renders it soluble when water is added and in this condition it is a very easily digested food.

Mention should also be made of the cheese industry. Although this, strictly speaking, is not a casein industry in the same sense as the industries outlined above, yet the basis of cheese is casein and the industry is large and thriving. A reference work giving latest

methods in cheese production is listed in the bibliography at the end of this chapter.

Self-soured and acid caseins are finding application in the preparation of massage creams. The casein is usually put into solution with a weak alkali, such as borax, and the excess alkali neutralized or converted into a soap by the addition of a fat. This neutral casein mixture is then incorporated with the cream. It assists in the formation of the rolls of solid matter, produced by continued massaging after the cream has been rubbed into the pores of the skin, which are essential to the proper functioning of the cream.

It has been found that the lime-casein mixture produces an excellent sizing coat for the interior of barrels which are to be used as oil containers. Self-soured or acid caseins are mixed with lime and water and the mixture shaken in the barrel until the whole interior has been covered. The excess mixture is then drained out and the coat of lime-casein allowed to dry. This same mixture is often used to size plastered walls in preparation for papering. It has been found that wall paper sticks better to sized than to nonsized walls. It has also been found that this mixture introduced into an insecticide solution used for spraying trees holds the poison on the sprayed parts longer and hence increases its effectiveness.

By-Products in the Manufacture of Casein

Although casein is the subject matter of this chapter, brief mention may not be entirely out of place of lines of research which seem to hold out most promise for the utilization of milk sugar and albumin. Their recovery has not progressed to anything like the extent of casein recovery, largely because no applications for

them on a large industrial scale have been found. Milk sugar, as such, seems to have a rather restricted field, being used principally as an ingredient in some infant and special foods and for the coating of pills, some of the so-called "sugar pills." But there is considerable promise in the development of fermentation products, alcohols, and acids, particularly lactic acid. In order to establish the best conditions for proper control of these reactions, the chemist and bacteriologist will have to work together closely. Such albumin as is now recovered is used largely for chicken feed, and as such does not command a very interesting price. Improvements in methods of recovery giving larger yields and a purer product will enable this material to compete with egg and blood albumins, for which there is a good market at fair prices.

Summary and Conclusion

The study of casein in preparation and in commercial application holds out great possibilities to the research chemist. In the first place, much valuable work remains to be done on the study of casein itself and of some of its most important reactions, especially the reactions with so-called hardening agents. There is little doubt but that when these reactions are better understood and controlled, many industrial possibilities will open up which are not dreamed of at the present time. The fact that tons of skim milk are annually wasted in this country, while we import almost twice the amount of casein we produce (figures for 1923 show 14,500,000 pounds produced and 26,489,992 pounds imported), is a direct challenge to the research chemist to cheapen the cost of manufacture of the domestic product, either by improved methods of man-

ufacture, which should at the same time tend to improve the quality of the product, or by more complete recovery and utilization of the by-products, milk sugar and albumin. In such work there must, of course, be coöperation extended by the interested parties. The Government has already coöperated to the extent of placing a duty of 2½ cents per pound on all casein imported into the United States. The coöperation of the manufacturer and farmer can be obtained when the results of research are translated to them in terms of dollars and cents, greater returns, and more profit from their business or product.

Reading References

Rogers, A. Industrial Chemistry. D. Van Nostrand Co., New York.
Sammis, J. L. Deckers Cheesemaking. Cheese Maker Publishing Co., Madison, Wis.
Scherer, Robert. Casein, Its Preparation and Technical Utilization. D. Van Nostrand Co., New York.
Acid Caseins. Bulletin 661, U. S. Department of Agriculture.
Casein, Its Utilization in the Paper Industry. World's Paper Trade Review, Volume 46, pages 281 and 657.
Tariff Schedule 15, Free List on H. R. 7456, December 30, 1921.

CHAPTER IV

THE CHEMICAL RAINBOW

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When we observe the great variety of colors that enter into the beautiful products of art and nature, contributing to our happiness, we realize for the first time how much less life would mean to us without them. We have, as a cherished inheritance from the past, a desire for color in our clothes and surroundings. Who, today, would be content in a world of black and white? The extent to which the expression of beauty is made possible by a harmonious blending of colors has been recognized throughout the ages. Almost from the beginning man has tried to imitate the beauty of nature by colors produced with dyes of vegetable and animal origin. The modern girl whose beauty and charm are intensified by the newest "creation" of the most popular hue and her ancient sister in her original skin colored to her taste by plant juices are chips off the same ancestral block. It is not improbable that Eve, the first woman, impressed with the splendor of Mother Earth's marvelously beautiful colored garb, selected her first cellulose gown after the same pattern.

Back as far as the recorded history of man goes, color plays an important role in the social and economic development of the human race. It has been used as a mark of class distinction and as an outward expres-

sion of human emotions, such as gladness, sorrow, religious fervor, and patriotism.

It is recorded in the book of Genesis, written probably about 1723 B. C., "Now Israel loved Joseph more than all his children because he was the son of his old age, and he made him a coat of many colors." Evidently, a coat of many colors was a garment highly prized and therefore appropriate for the expression of Israel's love. The colors blue, purple, red, scarlet, and yellow were known and used very early in the history of mankind.

There is abundant evidence that the ancients made woven fabrics of wool, silk, linen, and cotton with a considerable degree of perfection and dyed them in a variety of exquisitely beautiful colors and hues, using the coloring matter from herbs, roots, stems of plants, bark of trees, seeds, berries, nuts, lichens, blood of shellfish, insects, etc. Wrappings of mummies found in the tombs of Thebes, estimated to date back to about 4000 B. C., show that they were dyed with indigo and also bear witness to the fact that muslin of unusually fine quality was made at that early period. There are many other records showing that the use of dyes and the appreciation of colors continued down through the ages and came to us as a genuine inheritance. The writings of Homer, Theophrastus, Discorides, the elder Pliny, and others contain frequent references to the importance of color in the social and economic life of the peoples of different periods in the world's history.

Purple distinguished the Roman nobleman from the man of common rank. This purple color was called "royal purple" or "Tyrian purple" because it was obtained from the blood of a small shellfish or mollusk, which was plentiful in the waters near Tyre. It required about twelve hundred mollusks to give a little

over one gram of the extracted dye. Consequently it was expensive, one pound of dyed cloth costing the equivalent of about $170—and being beyond the reach of the ordinary Roman citizen, even if he had been permitted to wear it. Referring to the Roman purple, one early writer says: "It is for this color the fasces and axes of Rome make way in the crowd; it is this that distinguishes the Senator from the man of equestrian rank; by persons arrayed in this color are prayers addressed to propitiate the Gods; in every garment it sheds a luster; and in the triumphal vestment it is to be seen mingled with gold." Pliny also tells us: "Pearls may be looked upon merely as an everlasting possession; of everlasting duration, they descend from man to man, and they are alienated from one to another just like landed estates, but the colors which are extracted from the murex and purpura fade from hour to hour, and yet luxury which had similarly acted as a mother to them has set upon them prices almost equal to those of pearls."

The production of natural dyes and the art of applying them to fabrics continued as an important business down to the latter part of the nineteenth century, when synthetic dyes were produced and introduced in the markets of the world in competition with the natural products. About the middle of the eighteenth century, experimental science gained recognition and soon thereafter speculation was tempered by observed facts. The world was no longer satisfied to enjoy beautiful colors produced in Nature's laboratory; it wanted to know the secret processes by which they were produced. This curiosity led many a man to the desert sands of science to perish among the unknown. However, a chosen few possessing fortitude and perseverance came through, making it forever easier for others

to follow the trail. To these valiant souls we owe our progress in unraveling Nature's secrets. In certain instances complex dyes built up in Nature's factories were taken apart in the chemist's laboratory and their significant parts identified. Thus, the facts were secured which led ultimately to their synthesis. Soon, however, dyes which did not occur in the plant and animal kingdoms were discovered and applied. The majority of the dyes we use today have no counterpart in nature.

The Source of the Chemical Rainbow

Out of the bowels of the earth we obtain coal, a product as far removed from color as only black can be, and by the application of heat in a closed vessel we get from it, among other things, light oils (benzenes) and tar. The tar was formerly a nuisance, but now it serves as the chief source of very important substances such as benzene and toluene (in addition to those obtained in the light oils), naphthalene, phenols, and anthracene. These products are the chief crudes from which the intermediates for the manufacture of dyes are made. The three parent substances—benzene, naphthalene, and anthracene—furnish thousands of dyes capable of giving all the colors of the rainbow, and are now widely used to color food, clothes, shoes, paints, inks, paper, wood, and many other things which please us and thus contribute to our happiness and contentment.

Development of the Colors in the Chemical Rainbow

Sixty-nine years ago (1856), William Henry Perkin, then only eighteen years old, dared to think that he

could invent a method for the production of quinine from aniline. He treated a mixture of aniline and sulfuric acid with potassium dichromate solution and obtained instead of the quinine which he sought a black tarry smear in which he discovered "aniline purple" or mauve, the latter name being given to it by the French dyers who took kindly to the product and who were largely responsible for its industrial success. A year later the product was made commercially by Perkin and Sons at Greenford Green, near London, England. Thus a new era began in organic chemistry and the cornerstone of the synthetic dye industry was established. The average investigator would have discarded the smear that Perkin obtained and would have accepted defeat. The boy who was destined to pave the way for the development of the modern synthetic dye industry was made of quite different stuff. He had the ability to recognize the possibilities of his observation and the courage and perseverance needed to extract the dye and push his discovery to a successful conclusion.

While Perkin is justly credited with the discovery of the first synthetic dye, he was not the first to produce synthetic products which would color certain fibers. As early as 1771, Wolfe had produced picric acid by treating indigo, a natural dye, with nitric acid. This was a glimpse into a new world of thought and activity and it is not surprising that further discoveries of great importance did not immediately follow. The process was not practical but it had an important bearing on the subsequent work on the synthesis of indigo. It stimulated others to seek to discover the composition of indigo, as a result of which isatin was obtained from indigo. This discovery pointed to the possible relation between the indigo and the isatin molecules and

was an important contributing factor to the ultimate success in this field. As a natural consequence of the impetus given to the investigation of the nature of dyes, activity shifted gradually from the art of extracting and applying natural dyes to the study of the scientific principles involved in the synthetic production of dyes. Progress was slow. Very little of positive value regarding the exact composition of the natural dyes was known. The observations that had been made were so colored by superstition as to be useless. To account for the formation of organic substances on a rational basis in an age of superstition was practically impossible. It was then believed that special vital forces were actively responsible for the production of substances in living matter and that the same compounds could not be produced outside of living organisms.

In the face of the prevailing views of the time it required superb courage for Wöhler to announce, in 1828, that he had succeeded in making one of these products of vital forces, urea, from ammonium cyanate, which up to that time had been regarded as inorganic. This stupendous fact had a marvelous influence on the further progress of organic chemistry. In 1834 Runge discovered rosolic acid or aurin, the second synthetic product to be produced which had coloring properties, but it was too expensive to be of practical importance.

Perkin's discovery of mauve in 1856 unleashed the scientific forces of the time and the discovery of new dyes came in fairly rapid succession, particularly after a rational system of architecture of dye molecules had been formulated and adopted. Today there are thousands of such dyes known, many of which surpass in beauty, brilliancy, variety of hue, and fastness those fashioned by Nature. The coloring matter of the mad-

der root, alizarin; the dye extracted from the mollusks of Tyre, Tyrian purple; the coloring matter of the indigo plant, indigo; and many others are now produced synthetically.

A Significant Journey to the Fairyland of Molecules

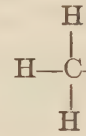
In the next several years following Perkin's discovery of mauve there were other related products made, but real progress awaited the discovery of a guiding principle to follow in building up complex molecules. The key to the treasure vault containing the mysteries of molecular architecture had to be found. Necessity has ever been the mother of invention. Something had to be done. Then occurred the most famous omnibus ride of all history—a journey to the fairyland of molecules. Late one fine summer evening Kekulé, then resident in London, hopped onto an omnibus and decided to ride outside as was his usual habit. The bus rolled on through a poorly lighted and now almost deserted section of the city which at other times teemed with life, and the tranquillity of his surroundings soon had a profound effect on the lonely man in communion with the great outdoors. As by the touch of the magic wand of some fairy goddess he was transported to the realm of the molecules and there before his astonished gaze the molecules danced and gamboled with impish glee. Now for the first time he was able to discern the nature of molecular motion and to see clearly the precise method in molecular madness. He saw the diminutive atoms frequently pair off and be embraced by larger atoms; he saw still larger atoms hold on to three or even four smaller atoms, while the entire group kept whirling in a giddy dance, the large

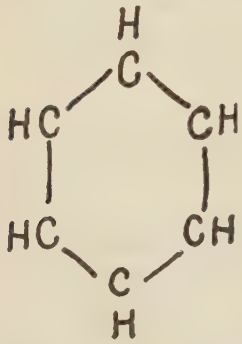
ones forming a chain. Gracious goddess of dreams, how wonderful thy powers! In due time Kekulé awoke and arrived home safely. Then, he tells us, "I spent part of the night in putting on paper at least sketches of these dream-forms." Out of this dream grew a system of constitutional formulas representing the structure or architecture of molecules of the open chain type. Later, in 1865, while sitting before his fire in his study at Ghent, Kekulé dozed off to the land of dreams once more and this time returned with the architect's specifications and plans for the benzene molecule. While in the dream he was again privileged to witness an exhibition tango dance by the molecules. Chains of atoms gamboled, squirmed, and twisted with snake-like motion before his very eyes. "But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke." Thus came into being one of the most fruitful of all the theories of molecular structure. It has been largely responsible for the rapid advances in organic chemistry and particularly for the progress in the synthesis of dyes.

The Architecture of the Chemical Rainbow

The dyes capable of producing the variety of colors we need are, for the most part, very complex substances and the creation of each has been an added triumph of research and technology. The structural idea in chemistry has been developed to a very high degree and is responsible for the rapid progress made. That "tropical forest primeval, full of the strangest growths, an endless and pathless thicket, in which a man may well dread to wander," which Wöhler saw

organic chemistry to be, has been cleared and in its stead there is erected a system of molecular architectural types beautiful to behold and marvelous in its possibilities.

The atoms are little systems which group together to form larger and more complex systems, not unlike our solar system, manifesting properties determined by their arrangement. One carbon atom unites with four hydrogen atoms and gives the substance methane. Architecturally this is  It is the fundamental unit in the chain system of carbon compounds. Carbon tends normally to group existence and under appropriate circumstances two or more of its atoms join together to form molecules of more or less complexity. There are two general systems of architecture, the open chain and the ring or closed chain. The benzene ring, consisting of six carbon and six hydrogen



OR as shown in Chart 1

atoms is the fundamental unit of the latter type. According to Kekulé it is a hexagonal structure. This is the basic structure in the architectural designs of dye molecules. The correctness of the above view has been

proved experimentally by several investigators at different times. The structural formulas for benzene, naphthalene, anthracene, and certain of the intermediates and dyes derived from these hydrocarbons are shown in Chart 1.

Relation of Molecular Architecture to Color

Color is a sensation caused by stimulation of the optic nerve, usually by light. The term "color" is often incorrectly used to refer to a colored substance or to a product which is capable of producing color. We manufacture and sell dyes and other colored substances which are pigments but not colors. All colored substances are not dyes. Only substances which are capable of imparting to fibers or other objects a more or less permanent property of transmitting or reflecting colored light are dyes. The degree of permanency of the color varies widely and is what is meant by "fastness." The kind of light reflected or transmitted by substances depends upon their chemical architecture or structure. Certain substances let all the light that reaches them as white light pass to the eye, and they appear colorless; others permit only a portion of the light to pass, and they are colored; while still others allow none of the light to get away, and they are black.

Just as the architect secures different effects in appearance and stability or strength by appropriate changes in his design of a house, so the chemist gets different compounds of varying stability and capable of producing a variety of colors by modifying the structures of the molecules. Certain groups of atoms are absolutely essential in the design of dye molecules. These groups or arrangements of atoms within the

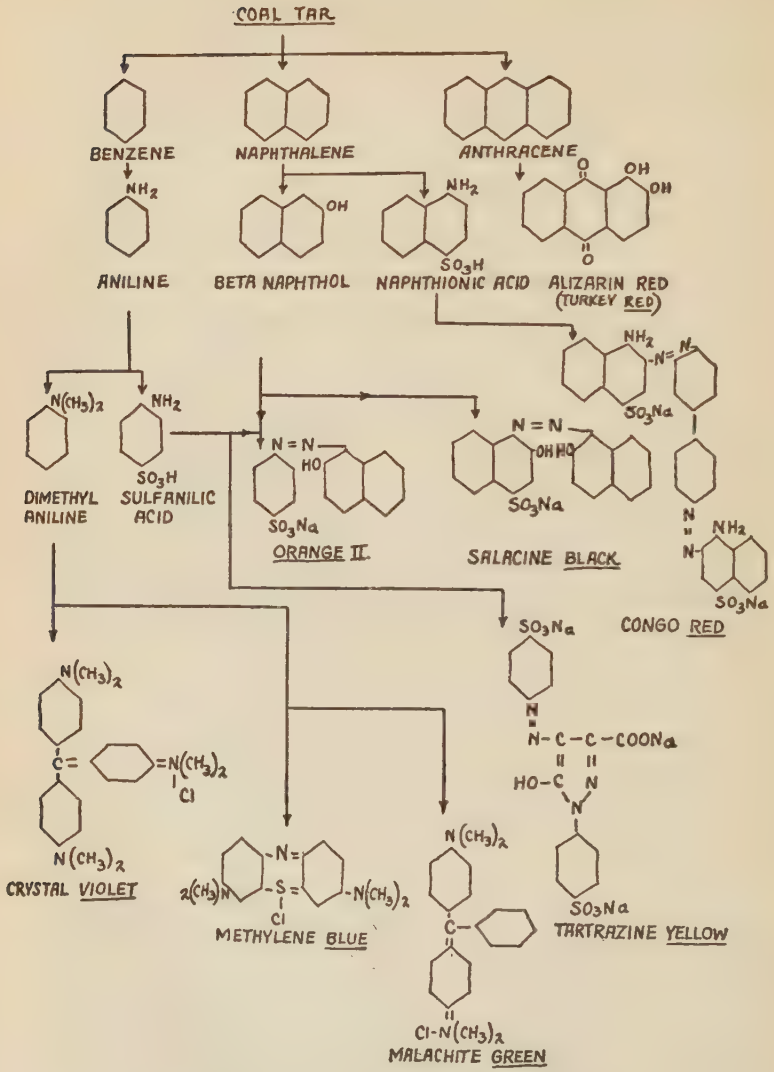


CHART I. — THE CHEMICAL RAINBOW SKELETON.

molecule are called "chromophores" and "auxochromes." The molecular structure containing one or more chromophores is a "chromogen." A chromogen may or may not be colored, but to be a dye it must have in addition one or more auxochromes.

The Chemical Rainbow as a Romance of Research and Industry

The chemical rainbow produced by synthetic dyes is the product of the union of Research and Industry. Where these two have obeyed the injunction to stand together for better or for worse, even under very trying conditions, the results have been marvelous. It required great perseverance on the part of research and extraordinary courage on the part of industry to win success. The chemist's faith in the ultimate success of the application of theoretical chemistry to practical problems inspired the confidence of industry to supply the necessary capital for development when there could be no assurance of immediate returns on the investment. It required about twenty years of intensive research to produce indigo, but the results have more than justified the cost. Thousands of other dyes and related substances have been discovered during the past sixty years and many of them are indispensable to the health and happiness of mankind.

The Aristocracy Among Dye Families

It is obviously impossible to give an adequate account of the romances of all the individual members of all the dye families in a work of this kind and in the allotted space; consequently we shall select for special consideration only the aristocracy among dye

families, duly conscious of the fact that in so doing important members of other families will not receive the attention which their value to industry merits. The families of dyes possess group characteristics which set them apart from one another and the resemblance in molecular architecture among individual members of each class is the basis for the classification, even though the individual members give different colors. Each family name is significant of the special type of architecture of the molecular group. The families entitled to special consideration among the "four hundred" are: the Azines, Triphenylmethanes, Azos, Anthraquinones, and Indigoids.

The Azines

The azines' claim to distinction is based on the fact that mauve, the first synthetic dye, is a member of the group. The family is characterized by a type of molecular architecture made prominent by a particular arrangement of two nitrogen atoms between two benzene nuclei. Such an arrangement of atoms is called a phenazine group and is chiefly responsible for the characteristic properties of the class.

The parent compound of this family is benzene. In 1825 Michael Faraday isolated benzene from coal tar and in 1834 Mitscherlich showed that it could be converted into nitrobenzene. This is made today in large quantities by treating benzene with a mixture of nitric and sulfuric acids. One hydrogen atom is exchanged by the benzene molecule for a nitro (NO_2) group from the nitric acid. As the exchange deal proceeds, water is eliminated. The sulfuric acid serves as the policeman of the reaction, taking the water into custody and thus preventing its blocking the deal by diluting the

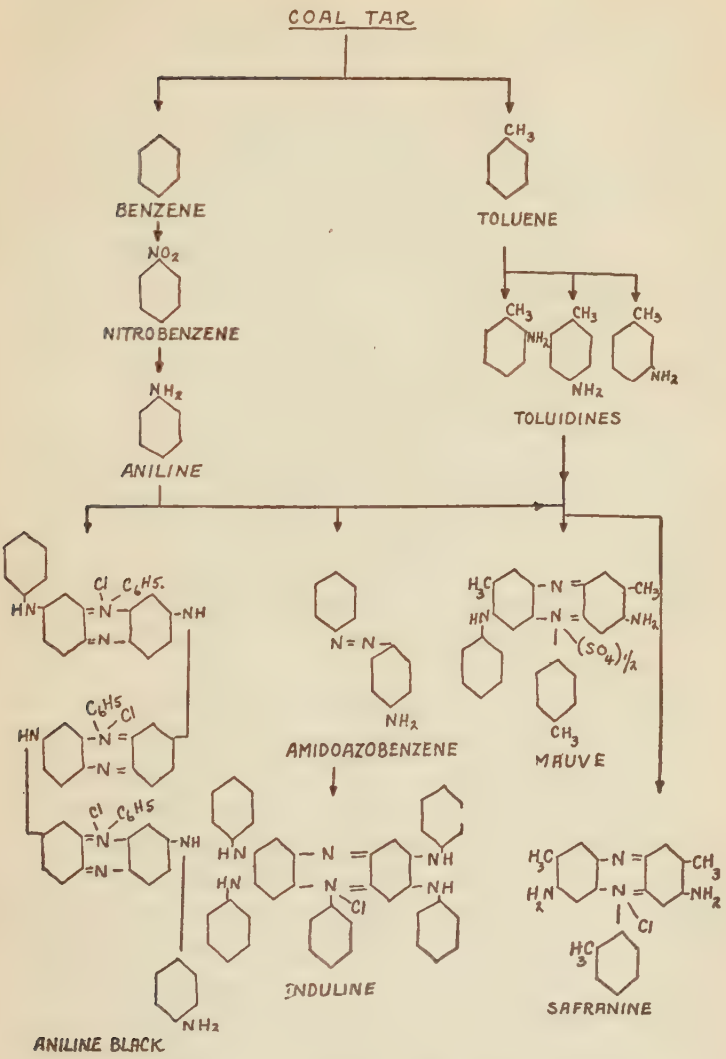


CHART 2.– THE MOLECULAR ARCHITECTURE OF THE AZINE FAMILY.

nitric acid. The nitrobenzene is then treated with iron, water, and hydrochloric acid and converted into aniline by swapping its oxygen for hydrogen supplied chiefly by the water. Aniline was first discovered by Béchamp in 1854 and was something of a stranger in the chemical world when Perkin selected it, in 1856, for the starting material in his proposed invention of synthetic quinine. He did not make the grade to quinine but reached mauve, the gateway to the synthetic dye industry. The aniline used by Perkin contained toluidine as an impurity, although he did not know it, and this made it possible for him to get his result. Had the aniline been pure he would not have obtained mauve.

Mauve is made by treating a cold mixture of aniline, toluidine, and sulfuric acid with a solution of potassium dichromate, filtering off the black product which is formed, and extracting it when dry, first with naphtha and subsequently with dilute alcohol. The alcoholic solution is evaporated to dryness to obtain the dye. It is of only minor importance as a dye, and is not used in this country.

Other typical examples of the azine family are safranine, induline, nigrosine, and aniline black. Safranine was discovered by Greville Williams in 1859 and is made by oxidation of a mixture containing equimolecular proportions of para-tolylenediamine and ortho-toluidine and then treating the resulting product with either aniline or ortho-toluidine. It is a reddish brown product dyeing wool a red color which is not fast to light. It also produces a red color on cotton which has previously been treated (mordanted) with tannin and tartar emetic.

Induline is made by heating a mixture of aniline, hydrochloric acid, and aminoazobenzene, the latter being also obtained from aniline. It produces a blue

solution in alcohol and is chiefly used to color varnishes and shoe polishes, for the preparation of printing inks, and in the manufacture of water-soluble induline.

Closely related to induline is nigrosine, a product whose chemical architecture is still unknown. It is made by heating a mixture of aniline, hydrochloric acid, and nitrobenzene. The resulting product is insoluble in water but soluble in alcohol. It is therefore known as "spirit-soluble" nigrosine. When treated with sulfuric acid it is changed to water-soluble nigrosine. The nigrosines are extremely important members of the azine family. They are used chiefly to color varnishes, shoe polishes and leather. Aniline black is another very important product obtained from aniline. It was discovered in 1860 by Lightfoot and others but its commercial success has been due to the combined efforts of a great many investigators. It is produced by oxidation of aniline hydrochloride (aniline salt) in the presence of certain catalysts like vanadium salts. It is usually produced directly on the fiber.

The Triphenylmethane Family

The discovery of mauve stimulated further research on the oxidation of aniline and in 1858 Verguin produced magenta. Later, Hoffmann was able to show that the product was a salt of a base which he called rosaniline. Here the hypothesis proposed by Kekulé was put to the test and it was shown that the basic architectural structure of the molecule was an atomic group arrangement called triphenylmethane. This is a methane molecule in which three of the hydrogen atoms have been exchanged for three benzene nuclei or C_6H_5 groups. This family includes some very important dyes. Magenta is made by oxidizing a mixture

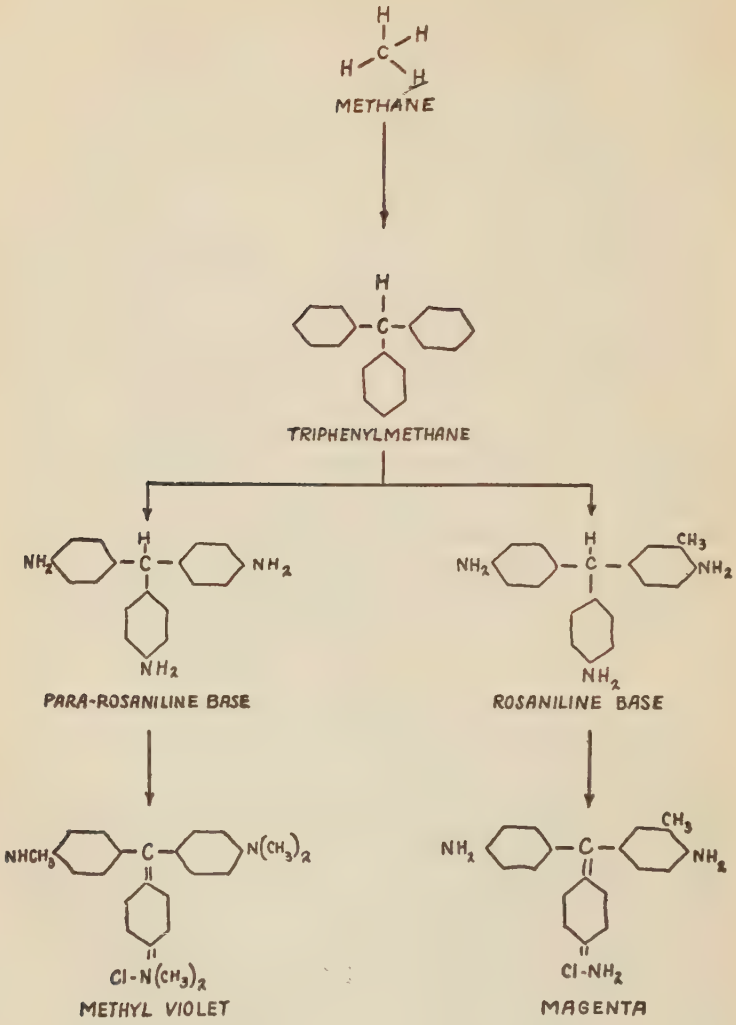


CHART 3 — THE MOLECULAR ARCHITECTURE OF THE TRIPHENYLMETHANE FAMILY.

of aniline, toluidines, and hydrochloric acid with arsenic acid or with nitrobenzene. It is used to dye cotton, wool, silk, and leather and also as a microscopic stain.

It was found that there were three amido (NH_2) groups in magenta and that by modification of these groups there could be produced dyes giving different colors. Methyl violet and malachite green are typical examples of dyes of the triphenylmethane family. Methyl violet is used chiefly to produce violet colors on wool, silk, rayon, paper, and cotton; in the manufacture of inks, indelible pencils, carbon paper, stamp pads, etc.; and as a microscopic stain. Malachite green is used chiefly to dye wool, silk, cotton, rayon, leather, paper, wood, etc.; for the manufacture of lakes; for the coloring of fats, oils and waxes; and as a microscopic stain.

The Azo Family

The dyes of the azo class are extremely important. They are characterized by the diazo (–N=N–) group and are made by combining diazo compounds with phenols, naphthols, amines, and derivatives of these compounds. They were first marketed about 1876 and immediately assumed a leading position in the synthetic dye industry. Almost every variety of color can be produced with these dyes. For the most part they are benzene and naphthalene derivatives. They are used to color wool, silk, cotton, wood, food, leather, and a great variety of other substances.

The Anthraquinone Family

There are two important branches of the anthraquinone family: the alizarins and the indanthrenes.

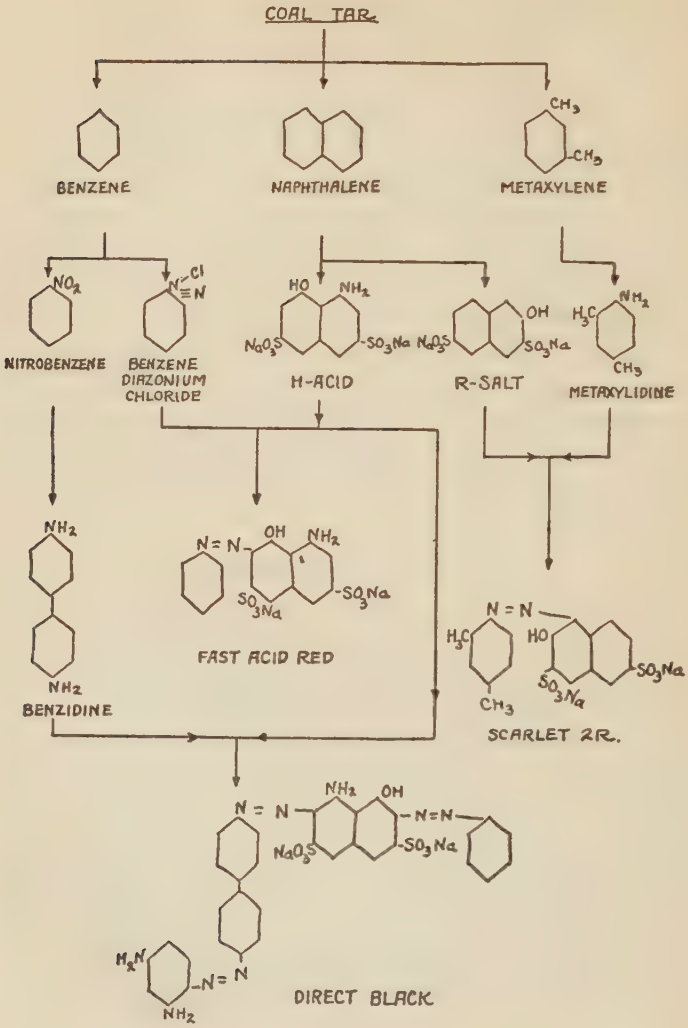


CHART 4. THE MOLECULAR ARCHITECTURE OF THE AZO FAMILY.

The parent compound of the family is anthracene, which was discovered in coal tar in 1832. This is converted into anthraquinone by substituting two oxygen atoms for two hydrogens in contact with the carbon atoms which serve as the bridges connecting the two benzene nuclei in the anthracene molecule. By treating anthraquinone with sulfuric acid a sulfonic acid is obtained. The sodium salt of this, when fused with caustic soda and subsequently treated with acid, gives alizarin, the chief coloring matter of madder. Alizarin was discovered simultaneously and independently by W. H. Perkin in England and by Caro, Graebe and Liebermann in Germany in 1869. This was the first of the natural dyes to be synthesized and marked a great triumph for chemistry. It soon displaced the product made from the madder root. It produces on cotton the famous turkey red color. Many other members of this branch of the family have been made.

The second branch of the family is much younger. The first member was discovered by Rene Bohn in 1901. Since that time many others have been discovered and all the colors of the rainbow can be obtained with them. These dyes are particularly important because of their ability to give extremely fast colors.

The Indigoid Family

Indigo is the most important member of this family. It is made in large quantities today, but it took about twenty years to develop a satisfactory commercial synthetic process. It is now generally manufactured from aniline which is made to combine with chloracetic acid and the resulting product is ultimately changed to indigo. Tyrian purple is now obtained from indigo

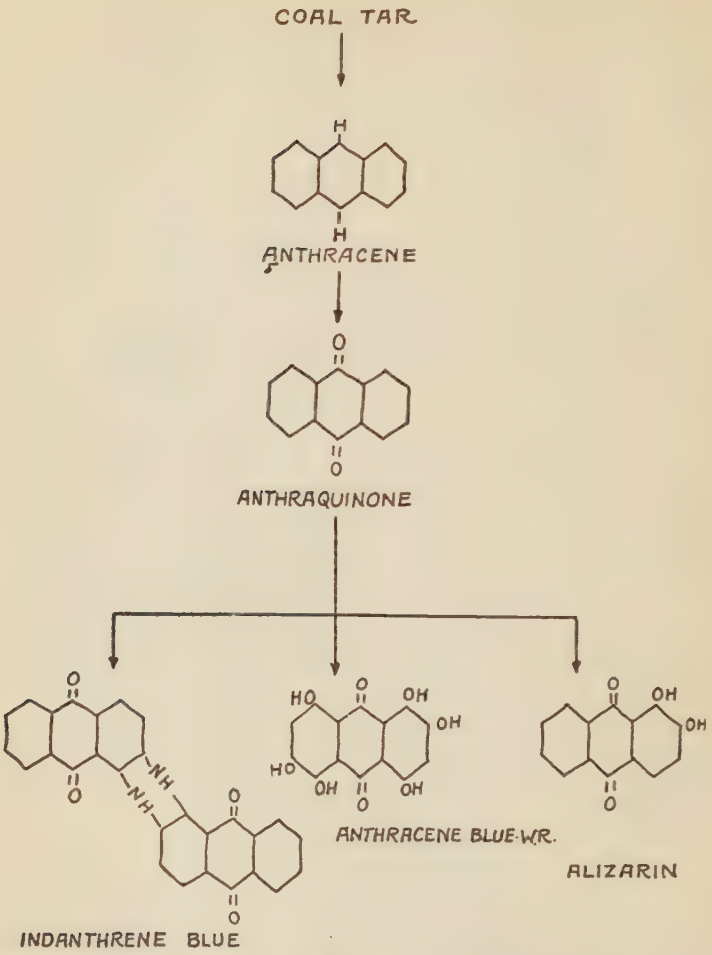


CHART 5- MOLECULAR ARCHITECTURE OF THE ANTHRAQUINONE FAMILY.

by treating it with bromine. Both of these dyes are identical with those obtained from natural sources.

Contribution of the Chemical Rainbow to Social and Economic Progress

The dye industry is closely related to many other industries. Although it is not a large industry in itself, it contributes to the success of large industries and is therefore a key industry. Any factor which disturbs its normal activity is likely to upset the economic balance in allied industries and endanger public welfare. The products of the dye factory enter the household of rich and poor, on silk and on muslin, in real furs and leather and in imitation products, in the necessities of life and in the luxuries. The knowledge gained in the research on dyes is used to good advantage in combating disease, the enemy of man. Research undertaken to solve the problems of disease and thus prolong human life is similar in character to that necessary for the continued success and progress of the dye industry. The dye industry is also indissolubly linked with the textile, agricultural, food products, pharmaceutical, perfume, explosive, leather, and rubber industries. Sulfuric acid, a product essential in the dye industry, is also indispensable in the production of fertilizers. To till the soil we need, in many cases, explosives which are made from the same intermediates and initial products used in the manufacture of dyes.

The dye industry is essential to national prosperity and safety in time of peace, and is the only security against national disaster in time of war. The existence of adequately equipped chemical plants is a surer guarantee against war than the presence of huge armies and navies which drain the nation's economic resources.

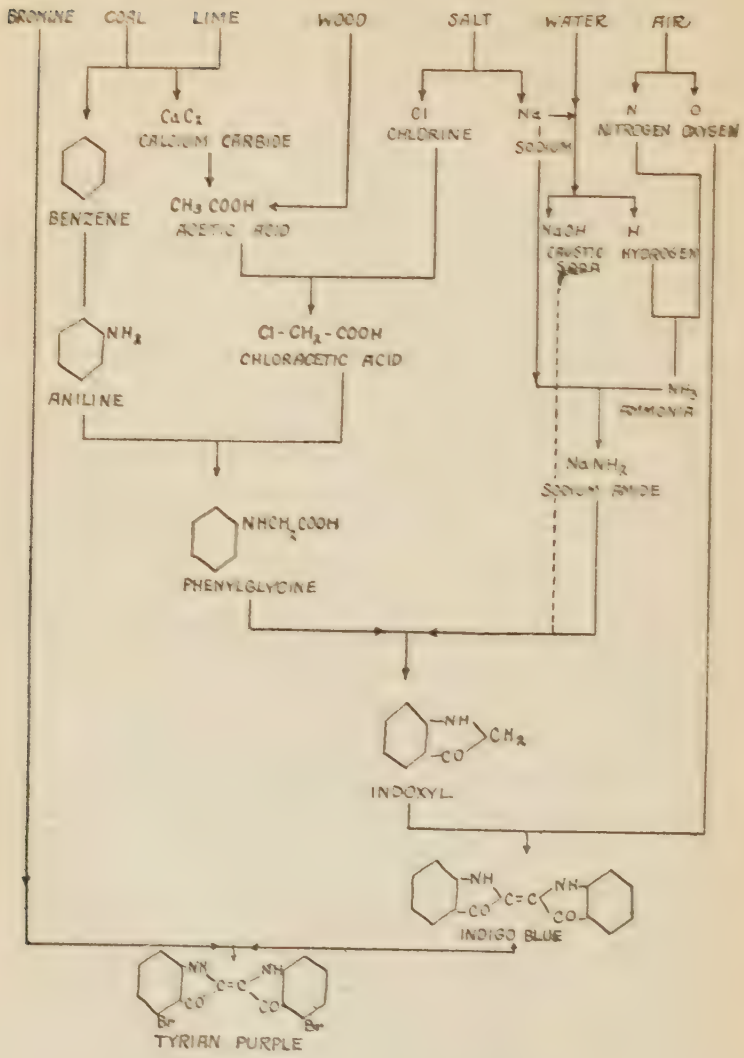


CHART 6— THE EVOLUTION OF THE INDIGOID FAMILY.

The Far End of the Rainbow

What awaits us at the far end of the chemical rainbow? For one thing, a better understanding of the internal mechanism of dye molecules and the causes of color. Through the coöperation of physical and organic chemists, more data concerning the behavior of dye molecules must be obtained, and the available data must be better correlated before we can know the exact relation between molecular architecture and color. For another thing, we must have cheaper and more efficient processes in order to utilize products which are wasted today. We must shorten the cycle of carbon dioxide to complex dye. The secret processes by which the plants convert carbon dioxide into the complex substances which give the delicate tints of color in nature must be better understood and approximated.

The use of dyes in medicine offers attractive possibilities for the future. Who will say that such dreaded diseases as cancer and tuberculosis will not ultimately be conquered by some one of the numerous armies of molecular soldiers in bright-colored tunics? We shall live to see that mamma mollusk, the lady bug coccus cacti, and all our other friends of the plant and animal worlds are given bodyguards of dye soldiers for some definite purpose.

Reading References

Armstrong. Chemistry in the Twentieth Century.
Findlay, Alexander. Chemistry in the Service of Man.
Findlay, Alexander. The Treasures of Coal Tar.
Martin, Geoffrey. Modern Chemistry and Its Wonders.
Slosson, Edwin E. Creative Chemistry.

CHAPTER V

CHEMISTRY AND ITS APPLICATION TO THE CONFECTIONERY INDUSTRY

STROUD JORDAN

Chief Chemist, Henry Heide, Inc.

During the past few decades confectionery has been taken from the hit-or-miss column and placed on a surer foundation. But with all evidence in favor of chemical control, the old-fashioned candy maker still has calloused fingers and his thermometer is most likely broken or covered with cobwebs. Radical changes seldom take place overnight, nor can we expect confectioners to wait with outstretched arms for untried reforms, especially when most of their foremen have been raised in the old school of cook-book and word-of-mouth procedure. Progress goes apace in the industry and manufacturers are making haste slowly, which is as it should be. Every year adds converts to the idea of exact procedure, suitable research, and progressive development.

No living person knows just when the human race first discovered those three important divisions of taste, sweet, salt, and sour, nor their order of discovery. Perhaps John Stonehatchet, on his way over a mountain to bring home a bride, was confronted by a bear who disputed passageway, but, after the conquest of

mind over matter, passed on. We may as well suppose that John was scratched up a bit in the encounter and, while searching for spider webs to stop the flow of blood, discovered something the bear had been eating. Now John was a chemist, for his curiosity was aroused and he tasted the stuff. Perhaps the time spent awaiting the outcome of the experiment seemed long, but results justified the adventure. Man has ever been vain and John was no exception; he decided to put off the bride-hunt and took an armful of the sweet stuff to his neighbors. Maybe they burned him at the stake; or maybe they let the more adventurous try it out; and in the latter event we can picture the next issue of the "Stoneville Chemical Journal" carrying an extra slab which heralded the discovery of a new, sweet food. And maybe they placed a bust of John in the Hall of Fame, after he passed on. Perhaps this was the way they discovered the first "sweet," but whether our allegory is correct matters little, for confectionery dates its birth from the discovery of honey.

The huddling habit is responsible for centralization of population and this makes it necessary to collect, store, and transport the larger part of our food. In man's endeavor to supply sweets to the ever-increasing population the sugar industry has been developed. With it confectionery has developed, for the basis of all confectionery is sugar. But sugar is not all, for there are many other products which find use in the preparation of favorite confections. The surface of the earth is combed for inviting tastes, perfumes, and viands with which to make something exclusive, something individual, and something profitable to produce. For general information a list of the more common raw materials of candy making will be given, but it must be remembered that it is impossible to name them all.

Sugars: Maple, cane and beet sugars. Corn, cane, maple and sorghum sirup. Honey, invert sugars, malt sugars and molasses of all types.

Starches: Tapioca, sago, arrowroot, corn, and potato. Soluble starches, thick and thin boiling starches, converted and partially converted starches.

Fruits: Sun-dried, desiccated, candied, preserved with sugar, canned, evaporated, and fruit concretes and juices of all kinds.

Nuts: Cocoa beans, pecans, walnuts, filberts, peanuts, almonds, pignolias, brazil nuts, and coconuts.

Proteins: Gelatin, albumin and casein.

Fats: Cocoa butter, coconut butter, dairy butter, almond oil, peanut oil, and many other nut oils.

Milks: Natural, evaporated, condensed, and powdered. Cream, evaporated cream, and powdered cream.

Flavors: Fruit extracts, whole fruits, synthetics, imitations, and blends.

Colors: Colors which are natural in the product used, colors developed by the cooking process, added vegetable and added certified colors.

Miscellaneous: Pure water which contains a minimum of mineral matter.

A good steam supply, refrigeration, conditioning apparatus, and other incidentals which are more or less familiar to well organized plants of any nature whatsoever are also necessary in the confectionery industry.

Chemical Control

It will require but a glance at the preceding table to see that a systematic examination of all products is a necessity. One will require specifications on all raw materials and will need to develop rapid methods of analysis to be sure that the products which are bought will be satisfactory. These tests are not always as scientific as might be desired from a purely chemical viewpoint, but give an insight into the actual working of a product when placed under factory rather than laboratory conditions. The role which chemistry is

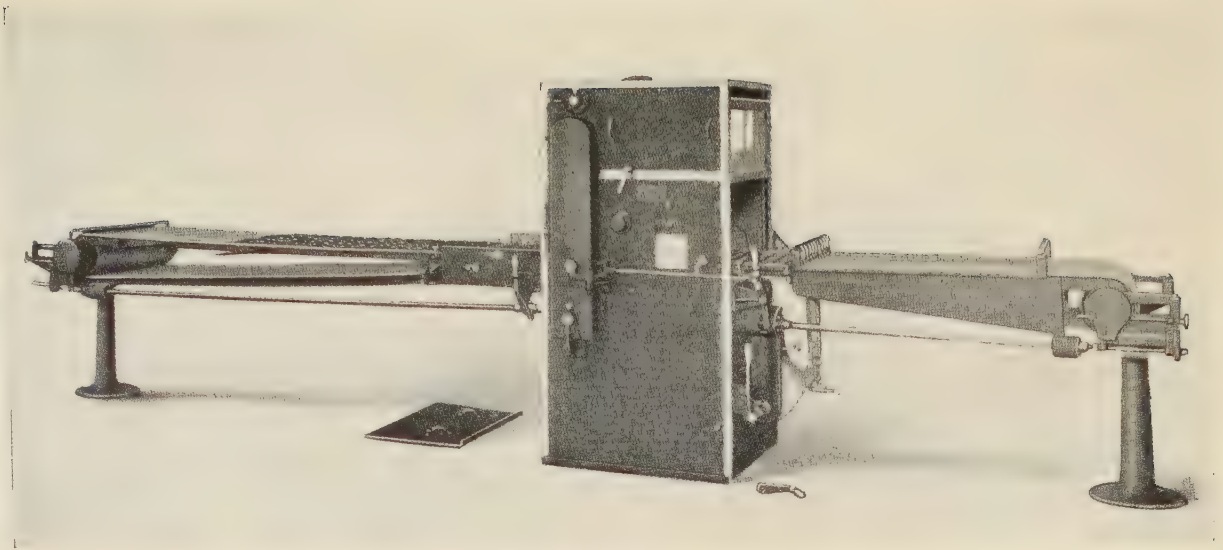
playing in the industry is rightfully classed as control work, and as the years pass, producing more and different kinds of products, it becomes more and more useful.

Development of New Products

Now, control work, though necessary in the production of standardized products, has to do with known materials and familiar processes. The progress of an industry is measured by strides made in the development of new products, along with new outlets for products already made. To develop new products requires research of a practical nature; blending together of all sorts and kinds of mixtures in an attempt to produce something new, something appealing, and something salable. Of course, one may say that any worker can do this, as it has been done in the past, but to obtain definite results in the shortest possible time and with the least possible cost, one must be able to predict the outcome before the actual product is made. As an example, take the mixing of a well-beaten albumin solution with sugar sirup at a temperature of 260° F. There is no trick in this, but if you believe the albumin (egg white) will work right, just remember what happens when an egg is dropped in boiling water. And still this very process is worked every day. In the production of nougat and certain kinds of marshmallow goods one wants the mixture to stand up, and albumin, if coagulated properly after beating, will stiffen up and hold a shape where the uncooked albumin would fall down. Here is where technical knowledge comes into play, and the man who not only knows how to mix but also why he should mix and what to mix is the man who makes the most progress. The hit-and-miss system of development is slowly giving way

to exact procedure, and to develop a definite material the chemist, who must be trained in practical confectionery manufacture, can take the analysis of a product or a proposed formula and predict with great success just what will happen under fixed conditions; can point out what not to do; and can actually go into the plant and do what he says can be done. To succeed in this work one must have practical as well as theoretical knowledge and one must also be so familiar with processes that he can make any of the several materials unassisted. The failure of development work may be traced to the failure of the chemist to translate laboratory results into factory practice, and this is largely due to inexperience in the production of the materials which he is trying to develop. "Overall" chemistry and "pipe-wrench" experience come in handy and ofttimes enable one to make a product without assistance and to make it better than the man who is regularly on the job; and this is what counts in the long run.

In finding new outlets for old products we are up against a far different proposition. The chemical examination of a product may give an insight into how it will behave, but time only, under varying conditions of handling and storage, will show definite results. Many products are held out of certain territory in the face of a brisk demand because humidity and temperature are adverse to the keeping of such products. The proper package, which will exclude humidity, can be made and correct blending and processing may produce a product which will stand the temperature; this is one of the greatest problems confronting the manufacturing confectioner today. Shelf-life of goods, proper packages, proper storage, and coöperation with the jobber and retailer so that stock is kept



Courtesy, Henry Heide, Inc.

Coater Used for Coating with Chocolate or Other Similar Material. Coating is Stirred Uniformly and an Even Temperature is Kept at All Times.

moving, are all being made possible by chemical research and development.

Definite chemical problems, which are being tackled every day, other than control and development, will be taken up under several general divisions, in order that a clear conception may be had of the actual application of chemical knowledge to problems which confront every confectioner.

Moisture

The success or failure of a product, either in eating or in keeping qualities, may often be traced to improper moisture content. The familiar hard candy, composed of sugars, flavors, and colors, may contain not more than a trace of moisture if it is to keep in good condition. Less than one per cent of moisture will make it stick, run together, discolor, and become a mess in a short time. The same candy with a slight trace of moisture will remain good for indefinite periods of time, except for the "graining," which is a natural tendency of sugar to crystallize and which cannot be entirely eliminated.

Marshmallow cream, cake fillers, and icings require very careful control of moisture, for each has a limit which may not be overstepped. If the finished cream is to remain uniform and not separate; if the cake filler is to carry and remain in storage without sweating and souring; and if the icings are to keep and set properly on the remelting, then the moisture percentage must be determined and strictly adhered to, but in some cases these facts are not yet well enough known to warrant the drawing of definite conclusions.

In fondant or sugar cream the keeping quality is directly dependent on moisture content. A fondant is made from concentrated sugar sirup which has been

boiled high, run through a cooler, and then beaten at a very high rate of speed. In this process the excess sugar is thrown out in finely divided crystals and at the same time some air is incorporated in the mixture. If the air is not distributed evenly, we may have large air bubbles formed which will give trouble later, and when the material is run through the depositor, where a given quantity is pulled into a chamber by the upward stroke of the piston and expelled by the downward stroke, more air may be pulled in if the pistons are leaky. In this operation it is almost impossible to exclude all traces of air, and when the warm fondant is deposited the larger air bubbles rise to the surface and lodge just under the skin of crystals which have dried out. If the original boil was not high enough, or if in subsequent handling excess moisture has been introduced, we shall probably have trouble. Packing goods with too much moisture in an air-tight container and storing in an excessively warm place will cause sweating and this sweat will condense on the surface of the container, being later absorbed by the surface of each individual piece. If this moisture is absorbed by the surface of a piece of candy which has an air bubble just underneath, the crust will dissolve and the air bubble will soon become a crater where excess moisture will collect and where mold and bacteria find a fertile spot for propagation. Or in a purely mechanical way the crater will grow larger with each sweating and the color in the piece of candy will gradually be forced away from the hole, leaving an ugly cavity which may be mistaken for fermentation.

In crystallizing any center the sirup must be pure sugar (sucrose) and water. Invert sugar above 2 per cent by sugar weight will cause trouble and goods crystallized in such a sirup will be subject to too fine

Courtesy, Henry Heide, Inc.

Beater Used for Holding the Proper Batch Temperature and for the Incorporation of Air.

crystals, slipping of crystals, and off colors. In this process the centers are immersed and kept covered with a sirup which is supersaturated and by properly regulating temperature and percentage any desired size of crystals may be had in the crystal jacket.

And so, if time permitted, we would find that all products which are made from sugar, either in part or wholly, must be watched carefully and checked often, if the proper ratio of moisture is to be present and the life of such goods is to be at the maximum.

Structure

In the preparation of sweet chocolate and sweet chocolate coatings it is necessary to incorporate powdered sugar. If the sugar is not ground fine enough and if the coating is not fined properly, the resulting material will be sandy and gritty. While the incorporation of sugar is a mechanical operation, it has its counterpart in the preparation of cream centers. This type of goods is composed of finely divided sugar crystals and saturated sugar sirup, and if the ratio is not proper we shall have trouble. In the remelting and casting it is necessary to use extreme care in holding the right temperature, and if the cream is not fluid enough at this temperature to be cast properly it is necessary to add just enough of a saturated sugar sirup. Structure study of such materials will show that where the temperature is too high the material will spot on cooling because of the extra high supersaturation of the sugar sirup, and the product will be gritty. The value of structure study of metals and alloys is well known; structure study of confectionery is just as important and just as valuable. For example, let's assume that we have trouble with a piece

of goods, that a structure study of the proper kind of material has been made, and that a photomicrograph of the very same goods has been made. All that becomes necessary is to make a photomicrograph of the sample in question and compare the two. Close observation will tell whether the structure is too coarse, too uneven, or if the color is not properly distributed. It will also show whether the trouble is due to sweating, bacterial or enzyme action, or to purely mechanical action in the remelting and casting. Two photomicrographs, when placed side by side, will produce unmistakable proof to anyone, whether or not he is familiar with the composition of the material, and the chemist can take such a picture and read the whole history of the material from its preparation.

Drying

In the preparation of confectionery a majority of the products have been handled in a liquid or semiliquid state somewhere down the line. These materials have been cast in molds, in order to make the several designs and shapes, and must be fluid enough to allow of charging and discharging the pump-bar. The molds are generally boards filled with starch which have had an impression transferred by dies to the starch. If the starch is to hold the shape of the impression it must be a careful blend of old or used starch and new starch. New starch will not hold the shape in a well-defined manner; if too much old starch is used the goods will dry slowly and in an unsatisfactory manner; if too much moisture is present in the starch the same fault will be apparent; and the starch itself must be kept under constant control. With the proper starch a piece of confectionery will dry on all sides; with

wet or sticky starch the only drying will be from the exposed surface; so it is evident that the starch is of the greatest assistance in taking out surplus water and then evaporating this moisture from its own surface. In other materials it will require warm starch in the molds if the cast material is to set properly and not take on too much starch; this is especially true with certain types of jelly centers.

After casting and molding it becomes necessary to eliminate excess moisture, and here we have our problems of determining the proper manner of drying all sorts of confections. Starch and gum goods will case harden and blow from too high heat and from forced drying; marshmallow and nougat goods, which have included air from the process of beating to lighten the product, will blow up if dried too quickly or at too high a heat; sugar cream or fondant will require little added heat, for it will set on cooling and being allowed to stand; jelly centers require no added heat, but stand in the starch molds until they jell properly; and the caramel type of confection must be handled in still another manner. The chemical nature of each piece must be known; the danger mark, where heating must stop, must be determined for each type of confection; and a change in composition of the same type will also necessitate a new study on proper drying.

By-Product Use

In any sort of manufacture a certain amount of perfectly good material falls by the wayside, perhaps because of appearance or perhaps from breakage. Or again the special use to which sirup has been put in coating and crystallizing work will leave a sirup which has absorbed enough color to make its further use im-

possible in the same process. It may be found that color will affect the shade of the product it was to be used in, and perhaps a new use may have to be found. If the color is simply a yellow one, developed by caramelization, it may be eliminated by decolorizing or may be neutralized by the addition of the proper amount of complementary certified color. All scrap or broken goods may be remelted and used again, but if there has been gum, starch, gelatin, or the like, used in the product, it must be kept off the filter press; it is not profitable to handle in this manner. On the contrary the simple yellow sirups may be decolorized for a cost not in excess of twenty-five cents per hundredweight of sugar, if the daily volume is great enough to warrant the installation of proper equipment. The proper place for each product must be determined, for the utilization of all material with the minimum of waste is the difference between bankruptcy and profits.

Shelf-Life

With finished goods the Sales Department gets busy, but to insure repeat orders it is necessary for the factory to be able to tell the salesman just how long each piece of goods will stand up in his particular territory. Just as the insurance companies reckon an average span of human life, and just as things of mechanical origin have fatigue points beyond which they will not last, so the confectionery industry is making and marketing products with an average individual life. The jobber as well as the retailer must be told of such life, and be warned to clear his stock every so often, if he is to keep salable goods. Nothing is permanent; confectionery is no exception, and it is a duty of the chemist to determine the actual life of a specific

product and to prolong such life if possible. The proper study of this problem will require years and then with each new product another problem arises, for its shelf-life will always have to be charted.

Flavors and Colors

Pure sugar and water will not make a piece of candy; such a product has no character other than a sweet and insipid taste. If, however, the proper flavor for the special type of goods is added, we have something which is pleasing to the taste. One eats largely by the eye, and if the product is to be salable it must have a direct appeal to the eye. This makes careful tinting of products necessary. Most people relish a piece of butter with a nice yellow color, which has been added, more than a piece of the white, scalded-milk type so familiar in certain rural districts. The chemist must keep an eye open for new shades, for pure colors, and for colors which have no effect on the batch in which they are used. To guarantee that succeeding batches will bear a family resemblance requires continual checking of color strength and close examination of materials used.

The Field of Development Work

This problem deals with manufacture of new products, utilization of old products, outlets for all products, and actual trouble shooting wherever and whenever a complaint is registered. The successful chemist must make the plant his laboratory and forget that the chemical department is closed within four walls. A good grounding of chemistry and much chemical experience are necessary, but actual factory experience is also necessary if the chemist would be of the most value

to any industry. This is the greatest field for the chemically trained mind in the whole confectionery industry, but one must be able to wear overalls with as much ease as a laboratory apron if he would succeed in this work.

Reading References

Berman, Matthew. The How and Why of Candy Making.
Browne, C. A. Handbook of Sugar Analysis.
Huasner, A. Manufacture of Preserved Foods and Sweetmeats.
Leach, Albert E. Food Inspection and Analysis.
Walter, Erich. Manual for the Essence Industry.
Whymper, R. Cocoa and Chocolate.
Chemical Abstracts.

CHAPTER VI

EARTHENWARE AND PORCELAIN

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The general terms, earthenware, semiporcelain, porcelain, and china, as applied to white or nearly white tableware, may be said to cover two large classes of ceramic bodies, the porous or absorbent, and the vitreous or nonabsorbent. The former stands for a product that has a more or less porous structure which permits the absorption of water or other liquids, and which, when examined in front of a light, shows practically no translucency. On the other hand, the vitreous bodies when immersed in water, in the unglazed state, absorb practically no liquid and when placed near a light source, show through the ordinary thickness of tableware, a distinct translucency.

Considered from this standpoint, the various terms like "semivitreous porcelain" and "china" are quite misleading. The term "china" is applied rather indiscriminately to such vitreous ware as the English bone china as well as to absorbent products. Such an expression as "semivitreous" porcelain has no meaning. A product either is or is not, vitreous and nonabsorbent. If it is not, it should be called earthenware and if it is, porcelain. As regards the absorption of water we need not be too exacting and we might establish a tolerance of say, one per cent of the weight of

the specimen being examined. Anything showing a greater absorption would have to be called earthenware. Hence, we shall call any white or nearly white ceramic body which is more or less porous and absorbent, earthenware, and any product of this kind that is nonabsorbent, porcelain. The former also would be only slightly or not all translucent, while the latter would be distinctly so.

The term "vitreous," which means glassy, must not be construed too literally. It does not mean that the ceramic body has become a glass, but only that it contains enough of a glassy matrix to cause the material to be dense and nonabsorbent. Earthenware likewise contains such a glassy cement but not as much of it. While the fracture of porcelain may resemble that of glass, it often appears to be of a stony character.

White earthen tableware originated in England, the product of the genius of Josiah Wedgwood, and was first known as Queen's ware. It represents the bulk of the pottery manufactured in this country as well as in Great Britain.

In speaking of porcelain we include a large number of vitreous ceramic products which we may know as French, German, Austrian, and Danish hard-fire porcelain, or English bone china, American porcelain, Belleek china, Chinese and Japanese, and Parian porcelain.

With the exception of the English bone china, both the earthenware and the porcelain bodies consist essentially of the same basic raw materials, which are primarily clay, feldspar and ground quartz. The differences in appearance and texture are due principally to the various kinds of clay used and the proportions of the basic constituents, coupled with very great variations in the firing or heat treatment.

The functions of the three primary constituents are easily understood.

The Clays

The clays are introduced for imparting to the mixture the degree of plasticity required in the molding and shaping of the fabricated articles. We have available for this purpose two kinds of materials, the kaolins and the ball clays. The former are divided into two groups, the primary and the secondary kaolins. The primary group consists of clays which are still in contact with the igneous rock from which they have been formed by the natural weathering agencies. The secondary clays are those which have been transported away from the site of formation, so that the deposits are no longer found in contact with their rocky origin. They are of much finer grain but do not fire to as pure and white a color as the primary kaolins, since they have taken up various impurities in the course of their transportation. But on the other hand, they are considerably more plastic.

The sources of well-known primary kaolins are Cornwall, England, which supplies the famous English china clays; Carlsbad, Bohemia; Meissen, Germany; North Carolina, and Maryland. Large deposits of secondary kaolins are found in Georgia and Florida.

The ball clays are very plastic and strong and are used to impart strength to ceramic bodies. They do not fire to a white color and become dense and vitreous at comparatively low kiln temperatures. Owing to their creamish or buff color the amount of ball clay must be kept as low as possible if a very white color is to be produced.

Chemically, both the kaolins and the ball clays are

hydrous silicates of alumina. The kaolins correspond closely to the formula: $Al_2O_3.2SiO_2.2H_2O$ with but traces of impurities, but the ball clays show comparatively slight deviations from this theoretical composition, in that they contain somewhat larger amounts of ferric oxide, lime, magnesia, and alkalies. The physical differences are very much more pronounced, due to the far greater fineness of grain and the larger content of colloidal material carried by the ball clays. The fusion point of pure kaolin is very close to that of platinum, 1755° C., and that of the ball clays somewhat lower. We must not get the idea that either the kaolins or the ball clays occur always as fairly definite substances, since this is not the case. Ball clays in particular are subject to wide variations in their physical properties. This is to be expected from the nature of clay deposits, but it makes the art of the potter one of constant surprises.

Feldspar

Feldspar is a mineral occurring in contact with igneous rocks, as dikes, and is a silicate of potash, soda, and alumina. The feldspars known as orthoclase and microcline, which contain principally potash and much less soda, are generally preferred in the making of pottery bodies. Pure potash feldspar corresponds to the formula: $K_2O.Al_2O_3.6SiO_2$. As might be expected from the alkali content of this mineral, it fuses at a comparatively low temperature, approximately 1270° C., and at still lower temperatures when the potash is replaced in part by soda or other basic fluxes. It should be understood, however, that the feldspars have no definite fusion point but undergo a gradual change from the crystalline to the glassy state, the rate of

which is dependent both upon the temperature and the time of heating. This sort of thing is typical of all the ceramic thermal processes. Upon fusion there is obtained a more or less translucent glass, which is quite viscous in the fused state and very hard when cooled. We can thus readily understand that it must be the function of the feldspar to provide the vitreous cement necessary to fuse together the other, more refractory constituents. According to the amount of feldspar used we can produce more or less glass for this purpose. At the same time this mineral, in the fused state, exercises a decided dissolving action upon the clay substance and the quartz contained in the earthenware and porcelain bodies so that at the kiln temperatures it enriches itself and continually increases the volume of the glassy matrix. Besides the purer forms of feldspar there are used also rocks high in this mineral but containing in addition some clay and quartz. Such a material is Cornish stone which is largely employed by English potters. It is evident, of course, that feldspar is always used in the ground state.

Quartz

The third major constituent of pottery bodies is ground quartz. This consists almost entirely of silica and may be obtained from sand, massive quartz rock, and quartzite. Its chief function is to reduce the shrinkage of the body mixture in drying as well as in the firing, and to impart to it a sufficient degree of rigidity so that during the vitrification process, when the kiln temperature is at its maximum, the fabricated articles will not deform by bending or "squatting." Quartz, though the most common of all the minerals, has peculiar properties when heated. It has the curi-

ous habit of being able to assume seven forms of crystallization and finally, at a very high temperature to fuse and become a typical glass. From the standpoint of the potter the most important crystalline modifications are the alpha and beta quartz, and the alpha and beta cristobalite. At 575° C., alpha becomes beta quartz with a sudden increase in volume. Upon cooling, at the same temperature the beta form again becomes alpha, with a decrease in volume. At temperatures above approximately 1370° C., beta quartz becomes beta cristobalite. Like quartz proper, this modification undergoes a reversible change to alpha cristobalite, but at 230° C. There are three more modifications of crystalline silica which go under the name of tridymite but which do not particularly concern pottery bodies.

An appreciable amount of quartz is dissolved by the fused feldspar, which eliminates it from any further crystalline changes. This solution process is of very great significance upon the final properties of earthenware and porcelain. Quartz thus dissolved and transformed into the glassy state assumes properties quite different from those shown in the crystalline condition. Taking as a criterion the thermal expansion, which is an admirable expression of the molecular changes, we find the mean linear expansion of crystalline quartz per Centigrade degree is 0.00001660. In the fused state the silica, now no longer quartz, possesses the lowest coefficient of thermal expansion of any known substance, or 0.00000055. It is obvious that such a tremendous change in the thermal expansion, a reduction to 3.3 per cent of the original value, must have a far-reaching effect upon the properties of the ceramic bodies. This we find to be true from the practical standpoint and our simple explanation clears up

many phenomena which have puzzled and troubled the potter. But not only the feldspar but the more readily vitrifying clays, the ball clays, as well do their part in dissolving some of the quartz. Unless present in excess, quartz contributes to the toughness of the bodies, but higher contents of the mineral lessen the resistance to sudden temperature changes, owing to the volume changes which the crystalline silica undergoes when being transformed from alpha to beta quartz or from alpha to beta cristobalite, and vice versa. Besides quartz or quartzite there are found in nature several forms of only partially crystallized silica, such as flint, chert, chalcedony, etc., which contain much amorphous material and hence behave differently from quartz in the firing process.

The final physical properties of ceramic bodies depend, hence, not only upon the composition but equally as much upon the characteristics of the specific raw materials introduced and upon the heat treatment to which the mixture is subjected in the kiln.

Body Compositions

In order that the reader may obtain some conception of the percentage compositions of different earthenware and porcelain bodies we shall compile some of them in the following table:

	English Earthenware	American Earthenware	European Hard Fire Porcelain	Japanese and European Soft Porcelain	American Table Porcelain	Bone China
Kaolin	43	38.2	50	19.0	38.50	30.0
Ball clay	18	13.1	....	15.5	6.00	....
Feldspar	....	13.4	25	30.0	16.0	....
Cornish stone	15	....	....	....	....	26.0
Flint (quartz)	24	35.3	25	35.5	38.00	....
Calcium carbonate	....	....	....	....	1.5	....
Bone ash	....	....	....	....	....	44.0

From these figures it appears that there is possible a wide range of composition, according to the type of product desired and the heat treatment contemplated.

Preparation of the Body

In the usual course of manufacture the kaolins are received by the potter in the washed state, having undergone a process of purification at the mine; the ball clays come in the crude condition; the flint and feldspar are finely ground. The materials are first weighed in the proper proportions and are then mixed and blended by being stirred up in water to form a suspension called slip. This may be done in suitable stirring tanks provided with paddles, or in revolving, cylindrical mills, called ball mills, in which a grinding action is produced by the presence of a large number of hard flint pebbles. The liquid is then passed through very fine metal sieves or silk lawns so that any coarse impurities may be completely removed. After this operation the slip proceeds over a series of electromagnets for the separation of any metallic iron. The purified slip is stored in large containers and pumped from these to filter presses similar to those used in the chemical industries. The object of this operation is to squeeze the water from the clay and to leave the latter in the form of round cakes within the plates of the press. These cakes or leaves of clay must then be kneaded and worked up in a machine, similar in construction to a sausage grinder, in which rotating knives cut up and compress the clay and force it through a nozzle in the shape of a continuous, round column of soft clay. This operation is called "pugging." The clay column is cut into convenient lengths and taken to the shop to be worked up.

The very lean mixtures used in European porcelain are not pugged as we have described it, but are kneaded and squeezed by a series of rollers operating on a revolving table in order that the maximum degree of plasticity may be developed.

Mixtures containing but small amounts of ball clay or none at all, are aged, that is, kept in damp cellars for from one to many weeks. With the use of larger amounts of ball clay this procedure is not so necessary and hence is often eliminated.

Molding and Shaping

The prepared mixture is now ready for fabrication. Three operations are available for this purpose, jiggering, pressing, and casting. The term "jiggering" is applied to the operation of the mechanically driven potter's wheel, which carries, properly centered, a plaster mold of suitable shape. The lower side of the piece is thus formed by the revolving mold and the upper by the application of a steel profile, fixed to a lever, called "pull-down," which can be raised and lowered. The mode of shaping the article consists in taking a lump of clay having about the desired weight, placing it on a moist plaster of Paris block and striking it with a flat surfaced hand maul. In this way a flat cake is obtained, called "bat." This is then thrown upon the revolving mold, the surface moistened with water and the pull-down lowered so that the steel profile shapes the upper side of the bat. In the case of a plate the revolving plaster mold produces the hollow or inside part of the article while the profile shapes the outside. Cups, bowls, and similar articles are made by shaping the outside with the mold and the inside with the profile tool.

Pressing is done by "batting" out a sheet of clay of suitable size and throwing it upon a plaster mold which shapes the inside of the piece. The outside is shaped and finished by hand with the use of simple tools. Large dishes, oval platters, and similar articles are made in this way.

Casting is the simplest but not the most rapid method of shaping pottery and is applied to more complicated shapes which cannot be made readily by jiggering. It consists of preparing a heavy but still quite fluid slip or suspension of the body constituents, through the addition of small amounts of silicate and carbonate of soda. This process represents a very pretty chemical reaction, since by the use of these chemicals it is possible to produce a suspension which contains but little more water than the body in the plastic state and yet is sufficiently fluid to be poured. The principle involved is that the clay substance of the body is deflocculated by the alkalies, that is, dispersed into its smallest particles. This condition is a sharply defined point which must be reached but not exceeded. According to the nature of the clays used, from 0.15 to 0.40 per cent of the alkaline reagents is necessary. The casting consists in pouring the suspension into plaster of Paris molds which absorb part of the water and cause a wall or shell of clay material to form around the inside of the mold. The excess of the liquid is poured off. Upon the shrinking of the body the piece releases itself from the mold.

The ware fabricated by these processes must be dried carefully. It is then finished, which means the removal of all blemishes.

The Firing

The dried ware is then placed in fire-clay receptacles,

called "saggers," which are carried into the kiln and built up into tall columns or "bungs." The first firing of the pottery is called the "bisque" burn. For American earthenware the temperature is carried to 1270° C., and for vitreous products to 1330° C. While in this country the bisque fire is brought to a higher temperature than the subsequent fusion of the glaze, in the case of the European hard-fire porcelain the reverse practice is followed, and the body and glaze are raised to a temperature of 1400° C., and higher.

In the firing of the body a number of chemical reactions and physical processes take place. First, both the mechanical and the chemical water of the clays must be driven off. At the higher kiln temperatures the feldspar begins to fuse and to exercise its dissolving action. The clay substance likewise decomposes into a new silicate, mullite, of the composition $3Al_2O_3.2SiO_2$. At first amorphous, this compound later begins to crystallize in the form of minute needles. Very refractory porcelains, like that from Copenhagen, contain a large amount of such crystalline material. The solution of the quartz grains becomes more and more vigorous as the temperature rises. At the same time the body contracts decidedly in volume, the so-called fire shrinkage. This is paralleled by the disappearance of the open pore space so that finally the body has become dense and nonabsorbent. In porcelain the final structure consists essentially of clay matter, decomposed into amorphous and crystalline mullite, some undecomposed clay, a considerable amount of glass produced from the fusion of feldspar and the clay and quartz it has dissolved, and lastly, the coarser quartz grains which have resisted solution. The amount of light translucency obtained is proportional to the amount of glass which has been produced.

The Glazing

The once-fired ware is glazed by dipping it into a suspension of materials which make up the glaze composition. The glazes are really glasses which have been adapted to the clay bodies to which they are applied. According to the nature of the product and the temperature to be reached various compositions are employed. Where brilliancy is desired at lower temperatures, boric acid and lead oxide are introduced. Since boric acid is soluble in water, it is necessary to render it insoluble by pre-fusing it in a glass which is ground and added to the glaze constituents. Such a glass is called "fritt." The higher the temperature of the glaze or "glost" fire, the simpler will the composition of the glaze become. Thus a high-fire porcelain glaze may consist of 16.6 per cent of feldspar, 9.8 of whiting, 23.2 of kaolin, and 50.4 of ground quartz. The factors which govern the selection of a glaze composition are its agreement with the thermal expansion of the body, fusibility, color, texture, range of fusion, and brilliancy. The heat expansion of the glaze must always be lower than that of the body. If this is not the case it will crack or "craze." The proper adjustment of the glaze to the body frequently offers a delicate problem. The firing of the glazes onto the bisque is greatly affected also by the kiln atmosphere, that is, by whether there is an excess or a deficiency of oxygen, especially in the case of glazes which contain reducible oxides, like lead oxide. Colored glazes are obtained with the use of various metallic oxides—like cobalt oxide for blue, chromium for green, iron and uranium for yellow, manganese for brown, etc. The oxide of tin is used for rendering transparent glazes opaque.

The firing of both the bisque and the glazed ware is usually done in round kilns whose diameters vary from sixteen to a little over eighteen feet. This operation is by far the most important one and at the same time the one most neglected, both from the standpoint of uniform heat distribution and fuel economy. Within the last few years continuous kilns have been built in several potteries and this type of firing operation is certain to receive more attention in the future. The kiln which is being considered more generally is a tunnel through which cars with well-insulated running gear are made to travel at a very slow and continuous rate. The furnaces are located at the middle of the tunnel and the combustion gases flow in the direction opposite to that of the cars. The temperature is maintained constant and as a car is removed from the kiln, another is introduced at the opposite end. Since the heat of the already fired ware and that of the combustion gases is fully utilized, the saving in fuel over the old type of kiln may be as high as 70 per cent. At the same time a better temperature distribution is attained. Other types of continuous kilns are also available with practically similar results.

Decoration

Decorations are applied either under or over the glaze. In the former case they are placed on the bisque after which the glaze is fired over them. Over-glaze colors are applied upon the finished glaze in one or more firings at a temperature usually not exceeding 775° C. While the under-glaze colors are of a more refractory nature, those used in over-glaze decoration are easily fusing lead borosilicates. The color pallet in the second case is very much richer, since many

oxides can be used, like those of antimony, cadmium, bismuth, and copper which would be too fugitive for the higher temperatures. At the lower heats it is possible also to employ such delicate colors as the rose, pink, and purple obtained from the use of gold. Metallic gold is used very largely for line decoration and stamping. Two kinds of gold are to be distinguished, the matt and the bright. The former is practically pure gold and requires to be burnished after firing on, while the latter is of a composition with a lower content of the noble metal, does not require burnishing, but is not as durable.

Colored decorations are applied either by painting or through the use of lithographic transfers, decalcomania, which are transferred from specially prepared paper to the ware. This type of decoration has reached a high degree of perfection and has been successful in transmitting the work of really noted artists. It is much to be preferred to the naive hand painting which at one time was generally considered to be the proper thing.

Technical Work in Pottery Manufacture

The manufacture of pottery thus presents a combination of craftsmanship, applied art, and technical science. Considered from the last-named standpoint it offers an interesting field of research in the solving of many problems which involve the control of the colloidal properties of the clays in their unlimited variations, their plasticity, their behavior at the kiln temperatures, the general phenomena of partial and complete fusion, the properties of the glasses employed as glazes, the more precise and uniform distribution of temperature in kilns and furnaces, and improved heat

economy. In addition, there must be considered the properties of other mineral substances, such as quartz, feldspar, the alkaline earth carbonates, the lead compounds, boric oxide, and the coloring metallic oxides. The subject of ceramics offers a difficult but fascinating field which calls for all the resources of the practical and the scientifically trained man. At the same time there is needed that appreciation of shop craft and industrial art which is necessary for useful service in these industries.

Reading References

Binns, C. F. Ceramic Technology. London.
Binns, C. F. The Potter's Craft. New York.
Bourry, E. Ceramic Industries. London.
Burton, W. Porcelain. London.
Sandeman, E. A. Notes on the Manufacture of Earthenware. London.
Searle, A. B. The Chemistry and Physics of Clays and Other Ceramic Materials. London.
Seger, H. A. Collected Writings. American Ceramic Society, Columbus, Ohio.
Journal of the American Ceramic Society, Columbus, Ohio.

CHAPTER VII

THE CHEMISTRY BEHIND ELECTRIC BATTERIES

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Chemist, Bureau of Standards

This is an electrical age. Through the development and utilization of electricity we are able to accomplish many wonders undreamed of a few years ago. The variety of uses of electricity is due to its ready convertibility into other forms of energy such as heat, light, motion, and chemical energy. As a result, we have a great many devices for converting electrical energy into any other desired form of energy. Thus, we have electric furnaces, ovens, lamps, and motors; and electricity is used in manufacturing many chemical products.

Most of the electricity used in our factories and homes is produced by large electric generators, called "power plants." These are usually operated by steam power supplied by the combustion of fuel, that is, by a chemical process. From them the electricity is distributed by wires (power lines) overhead and underground throughout the city and parts of the more thickly populated country. The power plants with their distributing power lines are called "power systems" and we have become very dependent upon them for our light, heat, and power.

Why Do We Have Electric Batteries?

It is obviously not practicable, however, for the power lines to be distributed everywhere. In places where electricity is desired and there is no power line available, some kind of an independent electric power plant is necessary. The electric battery is such a power plant. Thus, a battery furnishes the power to start and light your automobile. It lights your flashlight. In many isolated places, batteries are used to furnish current for lighting houses and running various electric labor-saving machines. Railroads use batteries to light signal lamps and operate mechanical devices for controlling trains. Railroad trains are lighted by batteries carried aboard. Freight trucks, mine cars, and other vehicles, including pleasure cars, are propelled by battery-driven motors. The telephone companies use great numbers of batteries for actuating the mechanism of their switchboards. Batteries ring bells, wind clocks, and operate recording instruments. Batteries are used on airplanes, airships, submarine boats, and submarine mines. For many kinds of work in laboratories and elsewhere, the current produced by an electric generator is not sufficiently steady, so that batteries are required. For the same reason, batteries are used by the radio public in enormous quantities. And even some of the great electric power plants are provided with huge batteries on which they rely to furnish electricity to part of their customers in case of emergency.

We have therefore become very dependent upon batteries because of their application to a great variety of everyday uses for which we need a convenient and reliable source of electric power. As a result, we have a host of kinds, sizes, and shapes of batteries ranging

from the miniature flashlight battery weighing a few ounces to that of the power station or submarine battery of many tons.

What Is a Battery?

Most of us are familiar with the outside appearance of the different kinds of batteries used for our flashlights, automobiles, and radio. The problem of designing and manufacturing them is a highly technical one which belongs to the specialized field of electrochemistry. The designing of the battery and the selection of materials for it constitute the work of the electrochemist, who must have a knowledge of electricity as well as of chemistry. Let us see what his field is like.

An electric cell is an arrangement by which chemical energy can be converted directly into electrical energy. A battery is simply a group of cells connected together. The Italian philosopher, Galvani, was the first to recognize that there is a relationship between these two kinds of energy. In 1786, he accidentally observed that freshly cut frog legs suspended by a copper wire upon an iron railing were subject to twitching movements when they touched the iron. He believed that the movements were caused by electric currents originating somehow in the animal tissue.

It remained for Volta, another Italian, a few years later to point out that a contact between the copper and iron was necessary for the production of an electric current, that is, there must be a complete circuit; and furthermore, that any electrically conducting liquid, called an "electrolyte," could be substituted for the fluids in the animal tissue. Consequently, in 1799, Volta made the first electric cell which consisted of plates of zinc and copper with a wet cloth between

them. In this cell, a small current was obtained by making a metallic contact between the two metals. While the current was small, it was possible by piling up a group of the cells in series to obtain a considerable electric pressure. This group of cells was called a "voltaic pile" and was the forerunner of our present-day battery.

The discoveries of these two investigators mark the beginning of the development of electric cells and really also of electrochemistry. Due recognition has been given them by the use of their names in deriving electrical terms. Thus, the term "galvanometer" was early given to the instrument used for the detection of small electric currents. We have also the electrical unit called the "volt," for measuring electric pressure, or voltage. We use synonymously the terms "galvanic" and "voltaic" when referring to the electrochemical process which occurs when two different metals in contact are dipped into any electrically conducting liquid. Such a combination of metals in a liquid is called a galvanic, voltaic, or electric couple or cell.

An electric cell is therefore a very simple affair. All that is necessary is two metals, called "electrodes," dipping into an electrolyte. One of the metals always has a greater tendency to dissolve than the other one, and this difference in tendency to dissolve is the basis of all voltaic cell action. While one metal dissolves, the other one tends to keep from dissolving or has hydrogen liberated upon its surface.

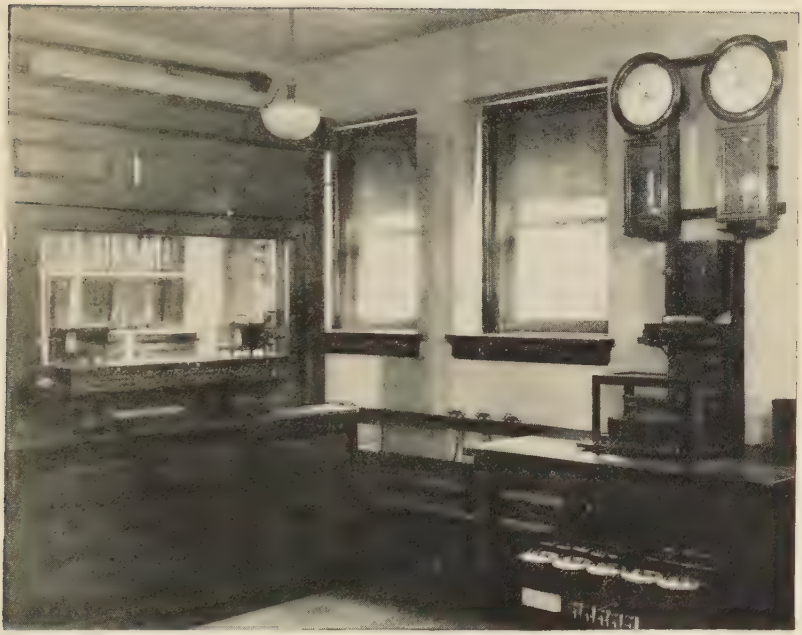
A voltaic cell may also result when two pieces of the same metal under different conditions are in contact with the same electrolyte. Thus, if two different portions of iron or steel come in contact with a film of moisture which serves as an electrolyte, an electric

cell is formed, one of the portions dissolves or corrodes, and we call it "rusting." The rusting or corrosion of iron and steel is really the electrochemical process of a voltaic cell. If a piece of zinc be brought into contact with the iron or steel, then the zinc will dissolve instead of the iron, which is in this way "protected" against corrosion. The zinc coating of iron and steel wire, pipe, bolts, etc., represents an industrial application on an enormous scale of the principle of the voltaic cell. Many chemists are busily engaged in the study of methods of preventing the corrosion of metals. But let us return to batteries.

Dry Cells

All the batteries of today are groups of voltaic cells. It may seem strange to say that the dissolving of a metal in an electrolyte is an electrical process. Yet this is true, because the metal atoms going into solution carry positive charges of electricity with them. So when a metal dissolves, it produces a flow of electric charges, that is, a flow of electric current into the solution. Thus in the common dry cell, the zinc metal container serves as an electrode and gradually dissolves in the solution contained in the cell during the flow of current. The zinc is consumed in the process and causes an electric current to flow into the cell.

But, you ask, how do we get out of the cell the electricity furnished by the dissolving zinc? All we need is carbon or a metal having a smaller tendency to dissolve than zinc has, dipping into the same electrolyte. In the dry cell, carbon is used because it is better than any metal for this purpose. Then when metallic contact is made between the zinc and carbon, the electricity flows out of the cell via the carbon electrode. We have



Courtesy, Bureau of Standards.

Automatic Apparatus for Controlling the Intermittent Tests of Dry Cells

then a complete circuit through which electric current will flow until the materials of the cell are exhausted. The amount of electricity that may be obtained depends upon the quantity of materials in the cell, that is, upon its size. The electrical pressure or voltage depends only upon the kind of materials and is independent of the size of the cell.

The Leclanché Cell

The common dry battery of today has been developed from the cell invented by Leclanché in 1868. It consisted of zinc and carbon mixed with other materials dipping into an electrolyte of sal ammoniac (ammonium chloride). The Leclanché cell is still used to a small extent for ringing door-bells. Its use is limited, however, because only small currents can be drawn from it. The current is small because hydrogen gas is liberated upon the carbon electrode and obstructs the flow of the current. The blocking of the current in this way is called "polarization," and in order to get any larger current from the cell, it is necessary to eliminate polarization, that is, to get rid of the hydrogen gas in some way. Any material which will combine with and therefore remove the hydrogen and stop polarization is called a "depolarizer."

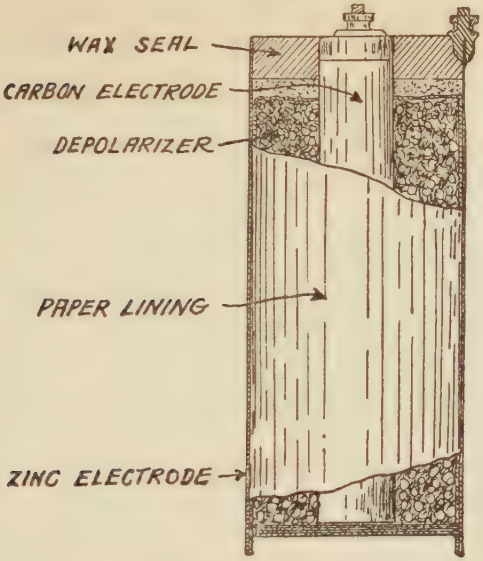
The search for good depolarizers has always been an important problem for the electrochemist. The depolarizer used in the Leclanché cell is a black mineral called "pyrolusite," which consists principally of manganese dioxide. It furnishes oxygen which combines with the hydrogen and forms water. Pyrolusite is mined in many parts of the world. Prior to the World War, the largest quantity suitable for use in batteries came from the Russian Caucasus. At the present time,

the battery manufacturers are using ore obtained from Africa, Brazil, and the United States. Manganese dioxide can be manufactured, but the artificial product is not as satisfactory for batteries as is the natural ore. The ore is ground in mills and mixed with coke carbon or artificial graphite to make a mixture which will readily conduct electricity. This mixture is then compressed into a firm block around the carbon electrode and is sometimes covered with a cloth bag.

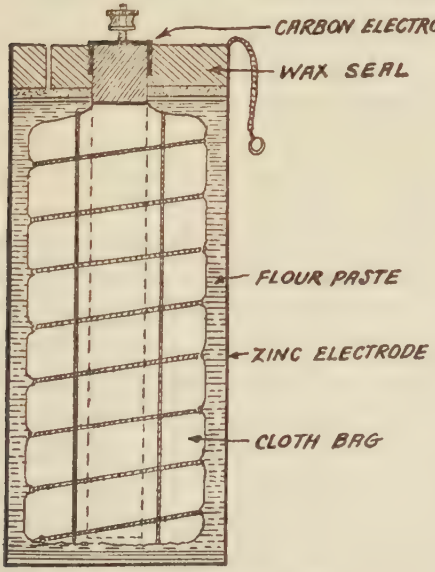
Many early attempts were made to devise a cell from which the electrolyte would not spill. These included the use of inert materials such as sawdust, asbestos, and various kinds of earth as well as jellies like gelatin, agar agar, and water glass. Gassner in 1888 produced the first successful nonspillable cell by the use of a jelly electrolyte. The term "dry cell" is really a misnomer because there must be a considerable percentage of water in the cell in order for the necessary electrochemical processes to occur.

Principal Types of Dry Cells

In the present types of dry cells there are two principal methods of keeping the carbon electrode and its depolarizer out of contact with the zinc. This is necessary, for otherwise the cell would be short-circuited and discharge itself. In some types, called "paper-lined" cells, the zinc container is lined with paper soaked with a solution of sal ammoniac. In other types, known as "bag-type" cells, the carbon electrode and its black depolarizing mixture are wrapped in a bag, and a flour paste containing sal ammoniac is poured into the space between bag and zinc. The flour paste becomes a stiff jelly. In this type, the bag is now being omitted entirely by some manufacturers with



SECTION OF PAPER-LINED CELL



SECTION OF BAG-TYPE CELL.

successful results. The paper-lined cells, of which the ordinary six-inch size is the most common, are used for ignition of gas engines, ringing door-bells, radio A-batteries, and for telephones. The smaller sizes, which are usually of the bag-type construction, are used mostly for flashlights and for radio B-batteries.

The growth of the dry battery industry has been linked with the development of devices requiring batteries for their operation. At the beginning of the industry, there was little use for dry cells. With the increasing use of telephones and the development of internal combustion engines, the demand for the six-inch paper-lined cells grew from about two million in 1899 to nearly eighty million in 1919. The development of the tungsten filament lamp for flashlights created an increasing demand for the smaller bag-type cells which amounted to nearly one hundred million in 1919. Since the popularizing of radio, the production of dry cells has increased so rapidly that an accurate estimate is difficult, but it is in the neighborhood of several hundred millions annually.

Standardization of Flashlight Batteries

In the natural growth of the flashlight industry, there resulted a great number of sizes and shapes of flashlight cases for which it was necessary to make an equal number of sizes and shapes of batteries. It became confusing to the purchasers and the manufacturers of batteries to have so many sizes. For the purpose of simplifying matters, the Bureau of Standards at Washington called a conference of leading manufacturers and representatives of the Army, Navy, Post Office, and other government departments, as well as some of the largest industrial users of dry cells. It was de-

cided to reduce the number of standard sizes of cells and batteries to those in most general use. This has resulted in great simplification and economy in manufacture as well as a saving to the consuming public.

At the same time that the sizes of batteries were standardized, the conference adopted tests requiring that batteries give a certain amount of electricity under specified conditions, depending upon the size of the battery. During the years since then, it is interesting to know that there has been a consistent improvement in the quality of the dry cells. The American public is therefore now getting better cells than ever before.

How Can Dry Cells Be Improved?

One of the most serious troubles with the dry cell is that it deteriorates, whether it is in use or not. This is due to the corrosion of the zinc by the sal ammoniac, to the chemical changes in the manganese oxides, to the loss of water, and to other causes. A cell which spoils rapidly is said to have a poor "shelf-life." Many schemes have been tried to improve the shelf-life. One of the common methods consists in making up the cell practically dry, with some mechanical provision for adding water or electrolyte to the battery when it is to be used, but these have not been commercially successful. Various additions of materials to the electrolyte have been found to improve the shelf-life; and much depends upon the character of the manganese ore used. The prolongation of shelf-life is, however, one of the problems upon which the battery chemists are still working.

On the average, probably not more than 25 per cent of the materials in a dry cell are utilized during the service life of the cell. There is therefore still much

room for increasing the efficiency of utilization of these materials. Aside from the low efficiency of the cell, the waste of materials is considerable because the cells are usually thrown away after use. This loss amounts to several hundred million pounds of material annually. If means could be devised for collecting these used cells, the chemical engineer could reclaim much of this material from waste.

Storage Batteries

There are two general types of batteries. The first type is the primary battery, of which the dry cell is the most common example. It is used once and thrown away. The second type is the storage battery or accumulator, which can be refilled with electricity from another source and used over again many times, and in which the electricity is stored as chemical energy.

The first successful storage battery was invented by Planté in 1859. It consisted of two lead plates in a 10 per cent solution of sulfuric acid. When an electric current was passed through the cell in one direction, chemical reactions occurred in the cell which were capable of delivering a current in the other direction. It required a great number of passages of current to produce electrodes which could deliver an appreciable quantity of electricity. It required months to produce suitable plates, and, since primary batteries were the only source of current for charging, the process of making the plates was an expensive and laborious one. Nevertheless, the Planté plate was so superior to others at that time that its development was continued. Since then more rapid methods have been found for making them and they are now quite extensively used for purposes where their weight is not objectionable. They

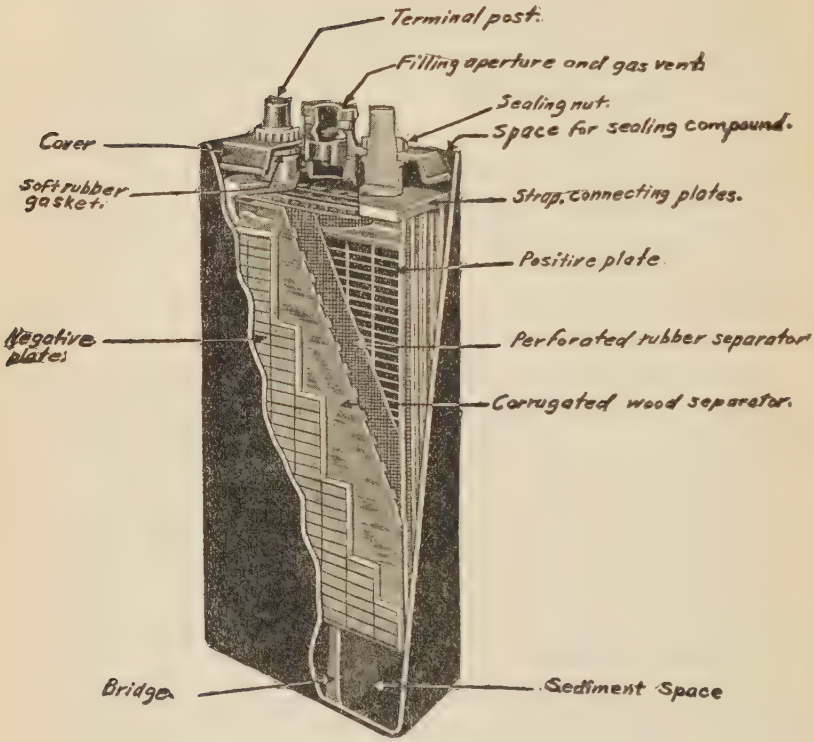
are also used to some extent for railway-car lighting because of their ability to withstand the severe vibration of the trains. Their weight, however, precludes their use for such purposes as radio and automobiles.

The success of the Planté battery and its excessive weight stimulated many chemists to investigate possible methods of making it lighter and of shortening the time required for its manufacture. The first successful attempts were made by Faure in France and by Brush in Cleveland, Ohio, about 1880, who initiated the development of what is known today as the "pasted plate."

The Pasted Plate Battery

In order to understand the difference between the pasted plate and the Planté plate, let us consider the chemistry of the storage battery. The Planté plates are made of pure lead. When current is passed through the Planté cell, the surface of one plate is converted into a layer of spongy lead; at the same time, the other plate becomes covered with a layer of lead peroxide. These layers are called the "active materials" of the plates. Their amounts determine how much electric current can be drawn from the cell. On continued use of the Planté cell, the active materials grow in thickness at the expense of the underlying lead.

In the case of the pasted plates, oxides of lead are applied in the form of paste upon a metal framework called a "grid." These oxides are then converted into active materials by passage of current. The framework is cast from an alloy of lead and antimony and serves both as a support for the active materials and as a conductor of the current. The alloy is stiff, and therefore resists mechanical stresses better than pure



SECTIONAL VIEW—LEAD-ACID TYPE OF CELL

lead, which is easily bent and twisted. Storage battery plates which lose their shape by warping are said to be "buckled." The paste is made of lead oxide (a yellow or red powder) and dilute sulfuric acid, or other solutions, such as ammonium sulfate. After applying the paste to the grid, it is allowed to dry and form a hard mass firmly imbedded within the network of the grid. The grid filled with the hard paste is then "formed."

The forming process consists in suspending the plates in dilute sulfuric acid and passing an electric current through them. The hard paste on the plate which carries the current out of the acid is converted into bluish-gray lead sponge; at the same time the paste on the other plate becomes lead peroxide of a chocolate brown color. The lead sponge plate is called a "negative" and the peroxide plate is called a "positive." The storage cell then consists of "negatives" and "positives" immersed in an electrolyte of sulfuric acid. Thin sheets of wood and perforated hard rubber called "separators," used between the plates, permit the current to flow but keep the plates from coming into contact and thereby short-circuiting the cell. The purpose of the separator is similar to that of the paper lining in the dry cell. Woods such as cedar, poplar, and basswood are used.

When the battery delivers current, the surfaces of both plates are changed into coatings of lead sulfate. The formation of this sulfate is often called "sulfation." At the same time that sulfate is formed, acid is consumed and water is formed. When the battery is charged, the sulfate is reconverted into lead sponge at one plate and into lead peroxide at the other plate. In this process the acid is restored and water is used up. It is for this reason that the strength of the acid

is greatest when the battery is full of energy, and smallest when the battery is completely discharged. We can, therefore, estimate the amount of electrical energy in a battery by measuring the strength of acid in it. This is done by means of a "hydrometer," which is a familiar instrument about battery service stations.

The Faure or pasted plates are used in far greater numbers than the Planté type. They are used in enormous quantities for making the batteries for starting and lighting the fifteen million automobiles in this country. While they are not as durable as the Planté plates, their lightness recommends them for all purposes where minimum weight is required. Plates as thin as fifty-thousandths of an inch have been made for airplane use. There is still much room for the chemists to improve the efficiency of utilization of materials in the storage battery and to increase its useful life.

Just as the flashlight industry led to the manufacture of many shapes and sizes of dry cells, so in the automobile and radio industries, perhaps an even greater variety of storage batteries has grown up. During the last few years there has been a considerable movement toward simplification through the efforts of the automotive engineers, the radio engineers, the manufacturers, the Army, the Navy, and other government agencies. At the same time, the methods of rating storage batteries and testing them are being standardized to the benefit of all concerned.

One often hears the question—Why must storage batteries be so heavy? This is because their chief components, lead and sulfuric acid, are, respectively, among the heaviest metals and liquids of commercial importance. As a result the storage battery is a heavyweight. Of course, multitudes of experimenters have

tried to make a lighter storage battery, but the pasted plate type represents the most successful attempt in this direction.

"Sulfation" of Batteries

One of the most frequent complaints of the motorist or radio fan is that his battery has "sulfated." The idea that a battery should not "sulfate" is erroneous. The formation of lead sulfate on the plates of a battery is a normal and necessary process required for the delivery of current, and the amount of sulfate formed is exactly proportional to the quantity of electricity delivered. Of course, a little sulfate may form when the battery is not in use, but this is mainly due to harmful impurities in the electrolyte. Since, therefore, sulfation is necessary for the production of current, it cannot be avoided if the battery is to be used.

If, however, a battery is permitted to remain in the discharged condition for a period of time, the plates become encrusted with a coarsely crystalline variety of lead sulfate. It is very difficult to redeem a battery from this condition and it is said to be "sulfated." Its condition, however, is not due to the formation of lead sulfate *per se* but to failure to charge the battery promptly.

Battery Dopes

Nevertheless, many people believe that sulfation is a serious defect of the battery, and are on the lookout for a means of improving it. This state of mind furnishes an opportunity for the dopester who has a new electrolyte for the removal of sulfation and otherwise "rejuvenating" the poor old batteries. He makes extravagant claims and charges fancy prices for his dope.

He even goes so far as to say that his magic liquid will charge the battery without the use of an electric current! Sometimes the dope is sulfuric acid containing such additions as nitric acid, that are very harmful to batteries; sometimes it is ordinary battery acid containing salts such as alum, Glauber's salts, or Epsom salts, which have no beneficial effect; and sometimes it is ordinary sulfuric acid, with or without coloring matter. Tests at the United States Bureau of Standards show that these dopes have no good effects and that some of them are really harmful. In any case, they are no better than the electrolyte ordinarily put into the battery at the factory where the battery is made.

The storage battery is so designed that nothing should be added to it except pure water to compensate for the loss due to evaporation. The addition of other materials should be carefully avoided. If the chemist finds a better electrolyte than sulfuric acid, the battery manufacturers themselves will undoubtedly be the first to use it. For the present, however, all battery users should steer clear of the dopes, of which there are dozens.

Dry Storage Batteries.

Many attempts have been made to produce an electrolyte for storage batteries that will not spill—that is, a dry storage battery. The usual procedure is to add to an ordinary battery several per cent of water glass (sodium silicate) which changes the electrolyte into the form of a jelly. This method was patented over thirty years ago and is "invented" again every few years. Others have made the electrolyte nonspillable by the addition of asbestos, sand, fuller's earth, and other similar substances, but the perform-

ance of a battery is hindered by their presence. The development of a successful dry storage battery is not promising because of fundamental difficulties, chief of which is the obstruction presented by the gas formed during charging of the battery. This gas is unable to escape from the jelly and therefore remains on the surface of the plates, where it offers a resistance to the flow of current. As a result, such a battery usually survives for only a few cycles of charge and discharge.

Charging Storage Batteries

The extensive use of storage batteries requires that some means be widely distributed for charging them; that is, that sources of direct current be readily available. Of course, the batteries on automobiles are charged by an electric generator run by the engine. Unfortunately for other batteries, nearly all of the current used in houses nowadays is 60-cycle alternating current, which is not suitable for charging batteries, because it reverses its direction 120 times per second. It is therefore necessary to have some means of converting the alternating current into direct or continuous current. The devices which accomplish this conversion are called "rectifiers."

A rectifier acts as a valve in an alternating current circuit, and permits pulsations of current in only one direction. There are three distinct types of small rectifiers on the market: the vibrating switch or magnetic rectifier which opens the circuit at every reversal of current; the ionized-gas bulb type, and the electrolytic rectifier, both of which block the current at every reversal of the current without opening the circuit.

The electrolytic type is becoming well known among battery users. It is an electric cell which permits cur-

rent to flow through it in only one direction; that is, it acts like a check valve to the flow of current. One electrode of the cell is usually lead or some other material which will permit the current to flow in either direction. The valve action of this cell is due to the character of the metal used for the other electrode. Aluminium and tantalum are two metals of the valve type in common use. The aluminium rectifier uses almost neutral electrolytes such as sodium ammonium phosphate or borax solutions and also weak acids like citric acid. The tantalum rectifier uses sulfuric acid of about the same strength as is used in batteries.

There are many interesting problems for the chemist and physicist to solve in the field of electrolytic rectifiers with a view to their improvement in endurance and efficiency.

Standard Cells

Since electricity is a commodity, there must be methods and units for measuring it. The kilowatt-hour is the commercial unit of electrical energy which your electric meter reads and is what you pay for. The size of the kilowatt-hour depends, in part, upon the value of the volt. The ordinary house-lighting current is 110 volts. You are also familiar with the 6-volt automobile battery and the 22.5-volt radio B-battery. The volt is one of the fundamental units used in all measurements of electricity. It is therefore of tremendous commercial importance that the value of the volt be correct.

The value of the volt is maintained by means of very carefully prepared cells of a special type called "standard cells." They are essential in all electrical laboratories. Their values are carefully determined by either

direct or indirect comparison with the standard cells kept at the United States Bureau of Standards at Washington. These cells have cadmium amalgam (an alloy of cadmium and mercury) as one electrode and mercury as the other electrode. The electrolyte is a saturated solution of cadmium sulfate and the depolarizer is a paste of mercurous sulfate. These cells must not be used for any other purposes because the least current drawn from them will spoil their value as standards.

The value of the saturated cadmium cell was chosen as 1.0183 volt at 20° C., by an International Committee which met at Washington in 1910. Representatives of England, France, and Germany brought their cells and compared them with those at the Bureau of Standards. The average value of the cells submitted by the four nations was taken as the standard. As a result of this conference, on January 1, 1911, the Bureau adopted the "International Volt" as represented by the saturated cadmium cell.

The portable standard cells commonly used in laboratories are like the internationally adopted cell, except that the solution of cadmium sulfate is not saturated. They are therefore called "unsaturated" standard cells. They serve as portable laboratory standards upon which the accuracy of all electrical measurements depend. The standard cells at Washington are compared with those of foreign countries from time to time, so that the relation between the electrical units of foreign nations and ours will be accurately known. They usually differ by only a few millionths of a volt. With proper care they last for many years. Some cells prepared at the Bureau of Standards in 1906 are still in excellent condition.

Carbon Cells

Since the electric cell can be made a very efficient mechanism for obtaining electricity from the chemical energy of materials, the question is often asked, why does not some chemist invent an electric cell in which coal may be consumed as an electrode and furnish electric current directly? This would be an ideal scheme, but many experimenters have tried it without any promise of success. The great difficulty is that there is no electrolyte which will dissolve the coal, the chief component of which is carbon. We shall therefore have to continue burning our coal and utilizing the heat for operating steam-electric power plants even though the efficiency of the method is low.

Reading References

Cooper, W. R. Primary Batteries. 1916.
Vinal, G. W. Storage Batteries. 1924.

The United States Bureau of Standards has published papers on batteries. A list of these publications can be had on request.

CHAPTER VIII

ELECTROPLATING AND ELECTROFORMING

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General Principles

In Chapter XIII of Volume I, reference is made to the electrolytic refining of metals and to the recovery by electrolysis of metals from solutions obtained by extracting their ores. In each of these processes the principal purpose is to obtain the metal in a pure state, and little attention is paid to the form or appearance of the metal deposits, which are subsequently melted and cast into shapes desired in trade. In electroplating, however, the purpose is to produce an adherent coating of one metal upon another in order to protect the underlying metal, or to produce some desired appearance or finish. Familiar examples of electroplating are nickel plating upon brass and steel automobile parts and silver plating upon tableware. Electroforming, a recently coined word, may be defined as the production or reproduction of articles by electrodeposition. This includes electrotyping, in which copper is deposited upon a wax mold to produce a replica of the original type form. Another example of electroforming is the production of molds for making phonograph records. The production of metal sheets and tubes by electrolysis is a branch of electroforming to which considerable attention is now being given.

The general principles of electrodeposition are so simple that at first glance it might seem as if there is little room for research or improvement. In order to deposit copper, all that is necessary is to have a solution containing some soluble salt of copper such as "blue vitriol" or copper sulfate, a piece of copper suspended in the solution to serve as an anode, and a piece of some metal upon which we desire to plate, which when hung in the solution, forms the cathode. When a direct current of electricity, such as the current from a dry cell[1] or storage battery is applied in such a way that the positive pole of the battery is connected to the copper anode, and the negative pole to the cathode, copper dissolves from the anode and deposits upon the cathode. If, as would happen under ideal conditions, the amount of copper dissolved from the anode is exactly equal to that deposited upon the cathode, the solution remains constant in composition, and the process may be continued until the anode completely passes into solution.

Actually, however, few if any electroplating baths operate in such an ideal manner. The anode may dissolve more rapidly than the metal is deposited at the cathode, in which case the metal content of the solution tends to increase, and if (as is always true with a copper sulfate plating bath) the solution contains an acid in addition to the metal salt, the concentration of the acid decreases. If less metal dissolves than is deposited, the metal content of the solution decreases and the acid content increases. If the salt used to prepare the bath, or the anode metal, contains impurities, these may accumulate in the solution. If any of the salts used decomposes, either as a result of the electrol-

[1]For large-scale plating operations, current is usually supplied from motor-driven generators, which have a low voltage, usually 3 to 12: but may have an amperage as high as 5000.

ysis or of the action of oxygen or carbon dioxide of the air, the composition of the bath is altered. Moreover, some of the solution always adheres to the plated articles when they are removed from the bath and is thus lost.

In consequence we find that in most electroplating operations the composition of the baths is changing constantly, even though gradually. If equally satisfactory deposits could be obtained, such changes in composition would be of little importance. Actually, however, the crystalline structure of the deposited metal, and hence its color, luster, strength, ductility, and other desired properties, are very directly affected by the composition of the solution and by other factors such as the temperature of the solution and the rate of deposition.

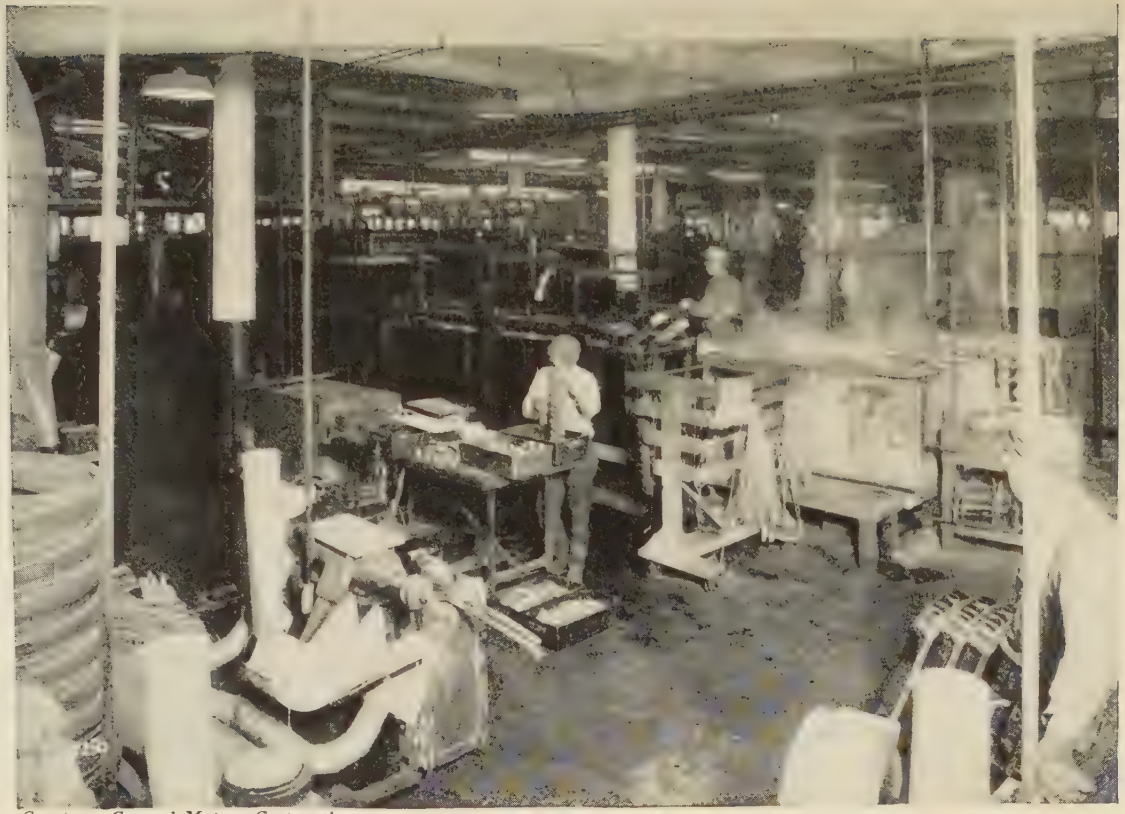
The above statements may well lead the reader to conclude, "Here, then, is an industry in which the service of chemists is indispensable, in order at least to analyze and control the composition of the solutions." Actually, however, although electroplating was one of the first industrial applications of electrochemistry, the industry both in this country and abroad was for over fifty years conducted almost entirely by rule-of-thumb methods. Platers learned by long and often very discouraging experience, that certain changes in the appearance of the deposits usually indicated the need of certain additions to or changes in their solutions. In consequence they were able, most of the time, to obtain satisfactory (though not always uniform) results. However, with the increased demands for plating upon a production basis, especially in large establishments such as in the automobile industry, it was no longer sufficient to secure good results "most of the time." Platers then came to the

realization that the way to avoid trouble is by prevention rather than by cure, in other words by keeping the composition of the solutions and conditions of operation constant instead of waiting for some defect to develop.

As a result, there has been during the past ten years, a great increase in the application of science, especially of chemistry, in the plating industry. Electroplaters have organized classes in numerous cities for instruction in chemistry, large manufacturing plants have employed chemists to coöperate with the platers in the control and improvement of their processes, and research laboratories supported by the industries, the universities, and the government have made extensive investigations upon plating processes. It requires considerable time to bring about changes in practice, especially where most of the units are small, as in the plating industry, and hence the results of this scientific work are just now becoming very evident. The next decade will probably witness changes and developments in electrodeposition which will seem almost revolutionary beside the progress of the past fifty years. To bring about such changes will require the services of many chemists, qualified for research, development, and control work; of progressive platers who have learned to apply the results of chemical analysis and research; and of manufacturers and executives with vision and faith.

Applications of Electroplating

In the minds of some persons, the idea of plating is associated with imitation, if not with fraud. Actually it may readily be shown that electroplating has rendered a great service to industry and to the nation,



Courtesy, General Motors Corporation

Typical Plating Room

Note the iron tanks to the right of the plating tank. These contain alkaline solutions used to clean the metal surfaces before plating.

both from a utilitarian and an artistic standpoint. By the application of zinc, nickel, or tin to iron, its corrosion may be prevented or at least retarded for considerable periods, thus permitting the use of iron and steel for many purposes instead of more expensive metals. Silver plating has rendered available to people in moderate circumstances the beauty and utility of silver tableware without the great expense and danger of theft that are involved in the use of solid silver. Most persons have heard of plating with nickel, silver, or gold, but few realize that there are important applications and may be still greater possibilities for the deposition of many other metals, including copper, zinc, cobalt, iron, chromium, cadmium, lead, tin, platinum, and brass. Some of these uses and possibilities may be summarized as follows:

Copper Plating

Copper plating is conducted either from an acid solution, consisting of copper sulfate and sulfuric acid, or from an alkaline solution, such as may be prepared by dissolving copper carbonate in sodium cyanide. (Many solutions used in plating contain cyanide, which is a deadly poison. Platers have learned to take the necessary precautions to avoid injuries from its use. It should not, however, be handled by amateurs.) The acid copper bath cannot be used for plating directly on iron or steel, as the iron dissolves and produces a film of copper "by immersion," which is usually nonadherent. (This may be readily confirmed by dipping an ordinary steel knife blade into a copper sulfate solution.) The cyanide copper solution is therefore used for plating on steel; and the acid copper bath is often applied subsequently for producing thicker deposits.

The latter bath is also used extensively for plating upon lead alloys such as are used for ornaments like book-ends, and small statuary. Copper plating is most frequently applied when ornamental effects such as "bronze finishes" are desired, which may be produced by the action of a soluble sulfide such as sodium sulfide, upon the copper. (Platers often refer to the product erroneously as "oxidized copper.")

Nickel Plating

Nickel is more extensively applied in plating than any other metal, and its uses are too numerous even to mention. It is used upon steel, brass, copper, zinc, and die castings. Its chief value depends upon the fact that nickel does not readily tarnish or oxidize upon exposure to the air. When a nickel-plated bumper bar rusts, this is not due to attack of the nickel, but to the fact that practically all nickel deposits contain fine pores or pin-holes, and hence moisture penetrates and attacks the iron, forming rust which exudes and stains the nickel. There is no simple commercial method of producing absolutely impervious deposits of nickel and thus securing permanent protection of iron, though recent developments and especially the use of relatively thick nickel deposits, have resulted in nickel plating which furnishes very satisfactory protection. In this connection it is interesting to know that the average thickness of nickel plating is usually only about one to two ten-thousandths of an inch (0.0001 to 0.0002-inch) while in special cases for protection, deposits of 0.001-inch or more are applied. (One ounce of nickel will cover about 1.4 square feet to a thickness of 0.001-inch, or about 14 square feet to a thickness of 0.0001-inch.)

In view of the importance of nickel plating it is natural that much research has been conducted on this subject in recent years. The details of procedure would not be interesting, but one point will illustrate the advantage of applying scientific methods to such subjects. Nickel-plating baths usually contain nickel sulfate (a green salt known by the platers as "single salt"), ammonium chloride (sal ammoniac), and boric acid. It has long been known that for favorable operation the nickel solutions should be just slightly acid, and many platers have used litmus paper to test the acidity. This is not, however, sufficiently sensitive to detect slight changes in acidity. Through recent researches more delicate methods of testing the acidity have been developed, and it has been shown that the best deposits can be obtained only within a narrow range of acidity. In any solution containing an acid, "hydrogen ions" are present, and the degree of acidity is dependent upon the concentration of these hydrogen ions. In an acid copper bath we may in a given case have a high concentration of sulfuric acid (a strong acid), and therefore of hydrogen ions, which concentration we may designate as "normal." In a satisfactory nickel solution the degree of acidity, or hydrogen-ion concentration is only from $\frac{1}{100,000}$ to $\frac{1}{1,000,000}$ that of an acid copper bath such as the above. In order to avoid the use of fractions and many ciphers, a system has been developed in which a number, known as the "pH," corresponds to the number of ciphers in this denominator. Thus a solution in which the hydrogen-ion concentration is $\frac{1}{100,000}$ normal, has a pH of 5;

and if the hydrogen-ion concentration is $\frac{1}{1{,}000{,}000}$ normal, the pH is 6. Most nickel plating is conducted in solutions with a pH between 5 and 6. Many nickel platers who formerly depended upon the use of litmus paper, or even upon guesswork, to regulate the acidity of the baths, now measure the pH by simple apparatus, and by adjusting it are able to control the quality of their deposits.

Cobalt, Iron, and Chromium Plating

These metals are of special interest because of their hardness. Recent experiments have shown that as measured by resistance to abrasion in the "scratch hardness" test, electrodeposited chromium is the hardest metal known. Cobalt has been suggested as a substitute for nickel, but thus far no advantages over nickel have been demonstrated that would justify the increased cost of the cobalt. Iron has little value for plating, as iron coatings will not resist corrosion. Iron deposition has been used to a limited extent for building up worn or undersized parts such as shafts, and for coating printing surfaces such as electrotypes.

During the past few years, chromium plating has attracted far more attention than that of any other element, and many researches are in progress, although it has not yet been applied to any appreciable extent on a commercial scale. The outstanding properties of chromium plating which warrant the present interest are its extreme hardness, and its resistance to atmospheric tarnish, to oxidation at moderately high temperatures, to the action of molten metals such as tin and zinc, and to many corrosive agents, especially oxidizing acids such as nitric acid. It is reasonably cer-

tain that in the next few years chromium will be used commercially for many purposes, for example upon printing plates where hard service is required; on dies and gages and other steel articles subject to abrasion, for which purpose it may eliminate case hardening; upon reflectors, where its resistance to tarnish will more than compensate for its slightly lower initial reflectivity than silver; and for many other special purposes. Just as with nickel plating, however, chromium coatings will not prevent corrosion of underlying steel if there are any perforations in the coating. The use of chromium plating for protecting steel against corrosion will therefore depend upon the production of initially impervious coatings, a very difficult task. If an impervious coating is once produced, the hardness of the chromium will reduce the danger of its penetration by abrasion.

Although for many years chromium plating has been known to be possible, extensive researches have been required to adapt it to meet specific commercial requirements, and much more work will be required before its use will become general. This fact emphasizes the need not only for specific discoveries, but also for long, patient researches and development work, such as can usually be best conducted by persons with broad scientific training.

Zinc and Cadmium Plating

These metals are very similar in their properties, especially in one respect that makes them valuable for protecting iron and steel against corrosion. When small areas of iron are exposed in the presence of nickel the iron readily corrodes, and in contact with copper, the corrosion of the iron may even be ac-

celerated. On the other hand zinc coatings may be visibly porous, and still the underlying steel will not corrode. This is because the zinc has a greater "solution pressure" or tendency to dissolve, than the iron, and hence in contact with moisture, a small electrolytic cell is formed, in which the zinc is the anode or dissolving electrode, and the iron is the cathode and is thereby protected. For this reason zinc coatings should be used wherever protection against corrosion is the primary consideration. As, however, the zinc itself readily tarnishes, it does not afford as pleasing an appearance as nickel.

Zinc plating, or "electrogalvanizing," is chiefly applied to parts subject to corrosion such as automobile rims, nuts, and bolts. Equally protective zinc coatings can be produced by zinc plating, by "hot galvanizing," and by "sherardizing."[1] The choice of the process for any given purpose therefore depends upon the relative cost and convenience of these different methods, and the requirements to be met.

Cadmium also protects iron against corrosion and because it is less readily attacked by air and moisture than is zinc, the deposits stay bright longer than those of zinc, and a given thickness of cadmium may protect the iron longer than the same thickness of zinc. Cadmium is, however, considerably more expensive than zinc, and before it can come into extensive use it must be produced more cheaply, or be shown to have some very special advantages for certain purposes. Considerable cadmium is obtained as a by-product of the zinc industry, and if there were more demand for it, the present price could be greatly reduced.

[1] In hot galvanizing, the iron and steel articles are dipped into molten zinc. In sherardizing the articles are heated in a closed drum with zinc powder, a portion of which adheres to produce a protective coating. In both methods some of the zinc alloys with the iron.

Courtesy, General Motors Corporation

Buffing and Polishing

To produce a high luster, much polishing of metals is required both before and after plating. This is done principally on rapidly revolving cloth wheels, upon the circumference of which the polish-

Lead and Tin Plating

Neither of these elements is applied very extensively by plating. Lead is especially useful in the chemical industries because it resists the action of sulfuric acid and certain other chemicals. Frequently storage battery fittings are plated with lead, to resist the action of the sulfuric acid in the batteries. During the war lead plating was successfully applied as a lining for gas shells. Tanks and pails for use in chemical works are often lead plated.

The tin coatings used on tin cans and on kitchen utensils are almost entirely produced by "hot dipping," in which process the metal articles are dipped into molten tin. It is possible to produce tin coatings by plating, but they are usually more porous and not so bright as the dip coatings. Frequently, however, small articles such as metal buttons, thimbles, pins, safety pins, and hooks and eyes, are coated with tin by "contact" or "immersion" processes. These are really electrolytic, although no current is applied from outside. In the immersion methods, the current which causes the tin to deposit, usually in a very thin film, is furnished by a small part of the metal object dissolving. In the contact method, small pieces of zinc which are in contact with the articles act as anodes and dissolve, thus producing the current that deposits tin on the articles. (In a dry battery a current is furnished in a similar way by the dissolving of the zinc).

Silver, Gold, and Platinum Plating

These expensive "noble" metals are often applied by plating, because thereby the desired appearance and properties can be obtained at a much less cost than if

the articles were made entirely of the expensive metal. The most common use of silver plating is upon tableware. The term "triple plate" does not mean that the articles have been silver plated three times, but simply that they have about three times as thick a deposit of silver as on some grade of cheaper quality. Roughly speaking, on "flatware," i. e., knives, forks, spoons, etc., of good "triple plate" quality, the average thickness of the silver is usually slightly less than 0.001-inch. As can be readily seen, certain parts like the bowls of spoons receive the hardest service and therefore usually wear through first. To counteract this tendency, most manufacturers "reënforce" the bottom of spoons and forks by applying a thicker coating of silver over the small area subjected to the hardest usage. Silver plating is also used on lamp reflectors because silver reflects a larger proportion of the light than any of the other common metals.

Gold plating is applied not only to many cheap brass articles such as collar buttons, thimbles, safety pins, and novelties, but also sometimes to articles that are made of a low carat gold alloy, and to "gold filled" articles. The composition of a gold alloy is expressed in "carats," representing twenty-fourths by weight. Thus an 18-carat gold ring contains eighteen parts of gold, and six parts of another metal, usually copper or silver. "Gold filled" articles are made from rolled sheets of metal of which, for example, the inside is brass, and the outside few thousandths of an inch on each side are 14 or 18-carat gold. By suitable choice of the solution and method of plating it is possible to produce various shades of gold, such as rose gold, red gold, green gold, white gold, etc.; and thus to produce desired colors upon a gold alloy which has a different color. In addition the gold plating of filled gold articles

serves to cover up edges and joints, where brass or solder would otherwise be exposed.

Of course the thickness of gold applied depends upon the cost and use of the article and within certain limits the plater and manufacturer can and will put on as much gold as the customer is willing to pay for. It is interesting to note that on many small cheap articles, the gold deposits, especially those produced by the "dip gold" process (an immersion process), are only a few millionths of an inch thick. One troy ounce (or twenty dollars' worth) of gold will cover about 200 square feet of surface with an average thickness of 0.000003-inch. Surely the plater deserves great credit for giving with so little gold a coating with a pleasing appearance, which often lasts as long as the article is otherwise serviceable. Persons who buy a "gold" ring for twenty-five cents should not, however, expect to find a dollar's worth of gold upon it!

Platinum plating is applied to a certain extent on jewelry, but the very great cost of the platinum (over one hundred dollars per ounce) prevents its extensive use. Chemists must frequently use platinum vessels to resist acids and exposures to high temperatures. If it were possible to produce by plating a dense impervious deposit of platinum of moderate thickness, it could be used to coat cheaper metals and thus save the great expense of platinum vessels. So far, however, no one has succeeded in producing by plating deposits of platinum that are entirely free from porosity.

Brass Plating

Brass plating is very extensively applied to building hardware and lighting fixtures of which the base metal is steel. Such practice is entirely justifiable, if there is

no misrepresentation, as it permits the use of the cheaper metals. For indoor use brass-plated steel usually gives good service, but it is not suitable for outdoor exposure, as the brass plating does not protect the iron against corrosion. (Those who wish to be sure of getting solid brass hardware and fixtures can satisfy themselves by the use of a pocket magnet, which will readily detect the presence of iron under the brass.)

Brass is deposited from a cyanide solution containing both copper and zinc. It is possible to deposit "alloys" of other metals, but thus far there are few uses for such alloy coatings. ("White gold," "red gold," and "green gold" deposits are really alloys of gold with nickel, copper, and silver, respectively.)

Applications of Electroforming

Electrotyping. In preparing such a book as this, the original type forms are usually "set up" by means of a monotype machine which casts individual letters, or a linotype machine which casts one line at a time. In either case the type consists of an alloy of lead, tin, and antimony, which is relatively soft. If many impressions were made from the type metal, the type would wear, and after the first few thousand, the impressions would become less distinct. In order to obtain better impressions and longer service, it is therefore customary to employ electrotypes.

The process of electrotyping is briefly as follows. A mold of the type form is made by pressing it into molding wax, a complex mixture which may contain ozokerite (a wax from Galicia), bees wax, and candelilla (a wax from Texas), together with rosin or rosin oil, paraffin, vaseline, and lampblack. The mold

is coated with graphite ("black lead") and is then hung as the cathode in a bath containing copper sulfate and sulfuric acid. The copper is deposited until it is about 0.006-inch thick, forming a "shell." This is separated from the wax and is then "backed up" by pouring type metal over the back, to a thickness of about $\frac{3}{16}$-inch. The plate is then finished to the desired thickness and dimensions.

For large editions, or for half-tone and color work, nickel electrotypes are usually prepared, because the nickel is harder than copper and also less attacked by colored inks. The process is similar to that of making copper electrotypes, except that the graphited wax mold is first hung in a nickel bath where about 0.001-inch of nickel is deposited, after which copper is deposited and type metal applied.

Electrotypes of cuts, half-tones, etc., are frequently made by "lead molding," in which process an impression is taken in thin sheet lead, upon which nickel and copper are then deposited to form a shell which is then separated from the lead mold. This process yields a better reproduction of very fine lines and dots, and also has the advantage that it is unnecessary to apply graphite or other conducting material, as the lead is a relatively good conductor. The lead mold is usually first treated with a dilute chromate solution, which produces a very thin film of lead chromate (chrome yellow) which permits the deposited nickel to separate from the lead.

During the past decade electrotypers also have realized the advantages of a knowledge of chemistry, and there has been a great interest in methods of analyzing and controlling the solutions. Research work is in progress to define the best operating conditions, especially for nickel electrotyping; and to specify the

properties of the materials best adapted to the industry. Even if no new processes are developed, an industry such as this can be greatly helped by standardization and the maintenance of uniformly high quality. There is, however, a need and field for research in electrotyping, including such problems as:

1. The production of a simpler molding composition that has the desired plasticity and other properties, and will not change in composition and properties by continued remelting.
2. The production of a satisfactory cheap powder which has better conductivity than graphite. Copper powder and other powdered metals are at present too expensive, and they tend to produce rough deposits.
3. Methods of producing plates of which the printing surface is perfectly flat. Although considerable progress has been made on this problem in recent years, a large amount of hand labor is still required to "finish" a plate to a plane printing surface.
4. The development of still harder printing surfaces for extremely long editions, or for hard service such as printing upon cardboard, leather, etc. For such purposes the application of chromium appears most promising.

Phonograph Matrices

When an artist or an orchestra prepares a phonograph record, the tones are recorded upon a wax form, by the method used in a dictaphone. Before replicas of this record can be manufactured for distribution and sale, it is necessary to make a metal form or "matrix," in which the plastic composition of which the record is to consist may be molded. This process involves several very interesting electroforming processes.

The original wax record is coated with graphite, upon which copper is deposited to form a "master plate," which is a negative of the original wax mold. This could, of course, be used as a form in which to mold the plastic composition, but if anything happened to it, the whole record would be lost, as the original wax mold is usually injured by the removal of the

metal deposit. Therefore this master plate is used as a form upon which one or more "mother plates" are deposited. Each of these plates serves as a mold from which the final "matrices" or stamping plates are made. The accuracy and faithfulness of reproduction by electrodeposition are so great, that good results are often obtained after several repetitions of the process, i.e., after several "generations" of plates.

In making these reproductions, the surface of the copper plate is treated with a silver cyanide solution, which produces a thin film of silver, and then with dilute tincture of iodine, which makes a film of silver iodide, that prevents the subsequently deposited metal from adhering permanently. The final stamping plates usually have a nickel surface.

Plate Printing

An electroforming process very similar to that just described is used at the U. S. Bureau of Engraving and Printing to reproduce part of the plates from which paper money and other securities are printed. Starting with an engraved steel plate as an original, a negative is made by depositing first nickel and then alternate layers of copper and nickel. On the original plate or "basso" all the lines are depressed, or in "intaglio," and hence on the negative plate or "alto" they are raised above the plane surface. This "alto" serves as a mold upon which an electrolytic "basso" or printing plate is deposited, and from which it is subsequently separated.

In plate printing, the ink is spread over the entire surface and is then wiped off from all the surface except the engraved lines. This process introduces con-

siderable abrasion, hence the plates do not last as long as in regular or "surface" printing. In order to produce a surface harder than electrolytic nickel, these plates have recently been chromium plated. The life of the plates has thereby been very greatly increased, and better impressions have been produced. This is important for money and securities, as it is much easier to detect counterfeits if all the genuine impressions are distinct and identical.

Sheets and Tubes

In recent years many efforts have been made to produce by electroforming, sheets or tubes, especially of copper, nickel, or iron. The results have been promising, and probably before long such processes will be in commercial operation. Electroforming is especially adapted to the production of very thin sheets and tubes, e. g., less than 0.01-inch thick. To produce thin sheets of copper or other metals by rolling is a troublesome process, and the expense increases as the thickness decreases. In electroforming, however, the expense is less per square foot for a thin sheet than for a thick sheet. The outstanding difficulties to be overcome in making sheet metal and tubes by electrodeposition, are the tendencies to form holes or pits in the deposit, and to form nodules or lumps upon the surface, which when of appreciable size are referred to as "trees." It is at least certain that successful operation of any such processes upon a commercial scale will require not only extensive investigations, but also eternal vigilance to maintain the favorable operating conditions. In other words the constant services of a chemist will be required.

Summary

The numerous uses and possibilities of various kinds of electroplating and electroforming can be well illustrated by considering the automobile of today, or perhaps better, that of tomorrow. The nickel plating will of course be most conspicuous, as it is used on the steel bumper bars, on the brass lamp trimmings, on the switch board and window fittings made of die castings, and on the hub caps that may be made of brass or sheet zinc. Less conspicuous but not less important is the zinc plating on the tire rims and fittings, and on many parts of the chassis. Copper plating may not be visible, but it is applied to many of the shafts and gears to protect certain parts during the case hardening operations. The copper gaskets may be made of sheet copper produced by electroforming, and if the motor is air cooled the radiator may be made of the same sheet copper. If it is water cooled, the copper radiator may be made by electroforming. The lamp reflectors, if made of steel, have been plated four times, that is, from a cyanide copper solution, an acid copper bath, a nickel solution, and a silver solution. If made of brass, the first two copper deposits are omitted. The future reflectors will probably receive, instead of silver, a coating of chromium to resist tarnish. Chromium may also be applied on some wearing surfaces to replace case hardening. It may also be used over nickel plating on bumper bars to increase the resistance to tarnish. Cadmium plating may be used on steel parts such as bumper bars, either alone, or preliminary to nickel plating. If in the manufacturing process some of the shafts are accidentally made under size, they may be built up by the deposition of iron. It is at least possible that in the future some of the

bearings may have a surface consisting of a deposit of a lead alloy, or they may consist of copper or some other metal with graphite included in it during its deposition. Then if the car is "de luxe," some of the inside trim may be plated with gold or platinum to match my lady's jewelry!

You will note that some of these applications of plating are not absolutely necessary to make the automobile run, but they may and do improve manufacturing processes, and help to make the car a thing of beauty as well as a utility. Whether the above mentioned and other possible applications of plating are realized, will depend largely upon the extent and cordiality of the coöperation between platers and chemists.

READING REFERENCES

Barclay and Hainsworth. Electroplating. 1913.
Bedell, W. L. D. Practical Electroplating. 1923.
Blum, W., and Hogaboom, G. B. Principles of Electroplating and Electroforming. 1924.
Hughes, W. E. Modern Electroplating. 1923.
Langbein-Brannt. Electrodeposition of Metals. 1920.
Partridge, C. S. Electrotyping. 1908.
Many articles on the principles and practice of electroplating and electroforming may be found in the Monthly Review of the American Electroplaters Society, the Transactions of the American Electrochemical Society, the Transactions of the Faraday Society, the Metal Industry (one journal of this name published in New York and one in London), the Brass World, and the publications of the U. S. Bureau of Standards.

CHAPTER IX

MILITARY AND INDUSTRIAL EXPLOSIVES

CHARLES L. REESE

Director of Chemical Engineering, E. I. du Pont de Nemours & Co., Inc.

The manufacture of modern explosives is essentially a chemical industry, and it is more than likely that all of the essentially basic explosive materials used today were discovered by chemists working in their laboratories in pursuit of chemical knowledge without any idea that they were going to find anything of practical value, and, least of all, that their researches would result in the discovery of new explosive materials.

Picric acid, probably the first chemical body known to be explosive, was discovered by J. R. Glauber (1604-1668) as a result of treating wood with strong nitric acid. It was known and used for many years as a yellow dye, but was not known to be explosive till about 1805, and was not put to use as a practical explosive until Sprengel discovered in 1871 that it could be detonated with a fulminate of mercury cap.

Guncotton was discovered by Schoenbein in 1845, and nitroglycerine by the Italian chemist Sobrero in 1846. These two substances are the basic materials used in modern dynamite and smokeless powder.

Trinitrotoluene and trinitroxylene were also known many years before they were utilized as explosives. All of these substances are what are known as nitrates

or nitro bodies and chemists often speak of the nitrogen content of these bodies when discussing their potential power. This is because nitrogen is easy to determine in analysis, but the essential material is the oxygen content because the explosion or detonation of these materials is largely due to internal combustion, or burning the oxygen supplied by the material itself.

Although they are stable substances under ordinary conditions, slight changes of conditions such as rise in temperature (heat) or mechanical shock render them unstable and they are said to decompose, explode, or detonate according to the rapidity at which the reaction takes place. Nitroglycerine has in its composition $C_3H_5(NO_3)_3$, enough oxygen (nine atoms in the molecule) to burn all of the carbon to carbon dioxide and the hydrogen to water, so it is a very highly detonating substance.

Industrial Use of Explosives

To the layman perhaps the term "explosives" suggests the idea of war, but no industry involving the production of explosives could exist if it were dependent on war business. It is true that war creates a tremendous demand for such materials, but fortunately war has no permanency and its occurrence usually involves the construction of special factories.

The consumption of explosives in this country for the purposes of peace-time uses amounts to between five and six hundred million pounds per annum, whereas the entire production of military explosives during the four years of the world war could not have exceeded two or three billion pounds, almost entirely made in factories specially built for the purpose which have since been demolished.

Explosives perform a much more important function in our modern civilization, for they are in the main used for constructive purposes rather than destructive. The production of military explosives such as smokeless powder and trinitrotoluene is only a small percentage of that of dynamite, black powder, and sporting powder.

Dynamite and black powder are necessary for our supplies of coal, iron, and other metals, and without it our railroads and great office buildings could hardly be possible. Sixty-three million pounds of dynamite were used in the construction of the Panama Canal; the great subways of New York and the present water supply of that great city were made possible by the use of explosives; in fact, the character of that city would be quite different, if its very existence were possible, without the use of dynamite. Railroad tunnels would be too expensive to build without the use of explosives and our railroads would have to follow rivers and the contour of the land and natural mountain passes. Not only stone for road making and building purposes, but also concrete is obtained by the use of explosives, and the labor supply for furnishing our population with these materials would be entirely inadequate without the successful use of explosives.

Millions of pounds of military explosives which were left after the war have been turned into peace-time explosives which are being used for the construction of modern roads, clearing stumps from land, and the draining of the land.

Since the field of explosives chemistry is so extended it is possible in this chapter to discuss only smokeless powder in any detail. It will be seen that the manufacture of sulfuric and nitric acids, alcohol,

ether, and diphenylamine are all chemical processes involved in this branch of the industry.

Gunpowder

The origin of gunpowder, which was the only propellent explosive known until the middle of the nineteenth century, is uncertain. The Chinese seem to have made use of it in warfare about 1232. The early use of gunpowder was confined to warfare and no use seems to have been made of it for blasting purposes for several hundred years. It was originally used in crude hand grenades and probably was at first of most use in striking terror into the enemy. Cannon were first used by the English in 1346 at the battle of Crecy, but may have been used a few years prior to this in the Hispano-Moorish war.

Until the end of the sixteenth century gunpowder was used in the form of fine powder or dust. To overcome the difficulty experienced in loading small arms from the muzzle with powder in this form, the powder was at the end of the sixteenth century given a granular form.

No marked improvement was made in gunpowder until 1860 when General Rodman, of the Ordnance Department, U. S. Army, discovered the principle of progressive combustion of powder and that the rate of combustion, and consequently the pressure exerted in the gun, could be controlled by compressing the fine-grained powder previously used into larger grains of greater density. To obtain a progressively increasing surface of combustion, General Rodman proposed the perforated grain and the prismatic form as the most convenient for building into charges. As a result of his investigation powder was thereafter made

in grains of size suitable for the particular gun. Powders of regular granulation, such as cubical, hexagonal, and sphero-hexagonal came into use, and finally for larger guns the prismatic powder in the form of hexagonal grains with one to seven perforations.

The object of the perforations was to obtain a more progressive rate of combustion. If a solid form of grain without perforations is burned, the burning surface begins to decrease immediately after ignition, and consequently there is a decrease in the evolution of gas. The decrease in volume of gas naturally limits the velocity of the projectile. With a perforated form of grain the burning takes place both on the exterior burning surface and within the perforations. There is an increasing production of gas until the burning surface of the perforations meets the decreasing exterior burning surface, at which time the powder grain is consumed.

A further control of the velocity of combustion of gunpowder was obtained in 1880 by the substitution of an underburned charcoal for the black charcoal previously used. The resulting powder, called brown powder because of its appearance, burned more slowly than the black powder, and wholly replaced that powder in the larger guns. During the Spanish-American war in 1898 the propellant used by us for ordnance was the brown prismatic powder.

For military purposes the use of black powder is now limited to bursting charges for shrapnel shell, to time fuses, and to priming charges for use with smokeless powder. It is still extensively used as a sporting powder, chiefly on account of its cheapness. This consideration and the fact that it does not require a detonator has led to its retention for blasting purposes. While greatly lacking in power as compared with mod-

ern high explosives, black powder has the advantage of being less shattering than most explosives, a great advantage when dealing with soft material which is desired in large lumps.

Black powder invariably consists of a mixture of sodium or potassium nitrate, sulfur, and charcoal, but for military purposes potassium nitrate is used instead of sodium nitrate because the latter is too hygroscopic.

Black powder, on account of its nature, was capable of only a moderate development for military use. It gives a relatively small quantity of gas in proportion to its volume, probably not over 50 per cent of the powder being converted into gas, and besides gives an objectionable volume of smoke and causes fouling of the guns.

Discovery of Guncotton

The discovery of guncotton by Schoenbein in 1845 and of nitroglycerine by Sobrero in 1846 opened up new ingredients for propellants, although the accidents attendant on the manufacture of these substances at first greatly delayed their general introduction. Schoenbein sold the British rights of his patent to John Halls and Sons of Faversham, England, who manufactured guncotton for a few months, but abandoned it in 1847 after a disastrous explosion. Six years later the Austrian Government took up the matter and General Von Lenk constructed some batteries in which guncotton was used both as a propellant and as a bursting charge for the shells. After two disastrous explosions in 1865 these experiments were abandoned. In 1865 Frederich Abel, working for the British Government, realized that the instability of guncotton was due to the difficulty of washing out the acid and intro-

duced the pulping process by which the guncotton was pulped in a beater or Hollander, and washed. Simple as it may seem, this was an important discovery, making the nitrocellulose safer to handle and store. Also the wet pulp could be compressed into blocks which were convenient for transportation and use. In 1868 Braun discovered that these wet guncotton blocks could be fired by a small primer of guncotton and the dry guncotton by a fulminate detonator. These slabs of wet compressed guncotton for many years were the standard explosive for military demolition and for mines and torpedoes until largely replaced by TNT and other high explosives.

Invention of Smokeless Powder

The first smokeless powder after Von Lenk's guncotton batteries was introduced by Schultze in 1865. It consisted of pellets of wood which were nitrated and then impregnated with barium and potassium nitrate. Volkmann five years later partly gelatinized the nitrated wood by treatment with a mixture of ether and alcohol. This use of solvent to colloid the nitrated wood cellulose must be regarded as having laid the foundation of the modern smokeless powder industry. A similar powder, E. C. powder, which was introduced in 1882 in England, consisted of partly gelatinized nitrocotton impregnated with a mixture of barium and potassium nitrates, and found immediate favor among sportsmen for shotguns and sporting rifles of low velocity. The gelatinizing of the nitrocotton by ether and alcohol caused it to burn more progressively.

The first military smokeless powder was Poudre B, named after General Boulanger, invented by the French engineer Vieille in 1886, while working in the

French government laboratories. The powder was adopted by the French Government. It was made by forming a dough of nitrocotton with alcohol and ether, which was then rolled out into sheets, cut up into strips, and dried.

Two years later, in 1888, Nobel introduced Ballistite, made by gelatinizing soluble nitrocotton of low nitration with nitroglycerine, and in the same year the British Government introduced Cordite, made by gelatinizing insoluble nitrocotton of high nitration with nitroglycerine and acetone.

The invention of Poudre B by Vieille, Ballistite by Nobel, and Cordite by the British Government was followed by many years of experimentation by the principal governments of the world.

The United States as is generally known was the last of the so-called World Powers to adopt smokeless powder for military use, which it did shortly after the Spanish-American War.

Smokeless propellants for rifled arms are usually divided into two classes, made with or without stabilizers, *nitroglycerine powders,* consisting of nitroglycerine and nitrocellulose, and *nitrocellulose powders,* consisting of nitrocellulose only. Both nitroglycerine and nitrocellulose powders consist of colloided masses of gelatinized nitrocellulose which have been pressed into ribbons, cords, or tubes, being subsequently cut into the desired lengths.

Chemical Stability of Early Smokeless Powder

As first made, the chemical stability of smokeless powder was not good, because the purifying and stabilizing of the nitrocellulose were not understood. Gradual progress was made along this line and later

stabilizers were added to the powder. These are compounds which are capable of reacting with the products of decomposition of the nitrocellulose and thus preventing them from increasing and causing rapid deterioration of the powder. While a great many stabilizers such as urea and amyl alcohol have been proposed and used, diphenylamine is the almost universal stabilizer now employed in an amount from 0.5 to 1.5 per cent with the exception that mineral jelly (crude vaseline) is used in Cordite, the British propellant, to the amount of 5 per cent. Introduced at first to reduce erosion, it was found to be a very effective stabilizer.

U. S. Government Smokeless Powder

The total amount of smokeless powder made in this country during the World War was greater than the amount produced by any other country. The powder used by both the Army and the Navy was adopted in 1900 after considerable investigation. The powder is of the nitrocellulose type, to which is added 0.5 per cent of diphenylamine as a stabilizing agent. The nitrocellulose has a nitrogen content between 12.50 per cent and 12.70 per cent, and is not less than 95 per cent soluble in a mixture of two parts of ether and one part of ethyl or grain alcohol.

Various Kinds of Nitrocellulose

Nitrocellulose is a material obtained by treating cellulose with a mixture of nitric and sulfuric acids. The term "guncotton" is frequently but incorrectly used to cover all the various kinds of nitrocellulose. Guncotton strictly has reference to a particular form

of nitrocellulose of higher nitration, usually between 13 and 13.4 per cent nitrogen content, which is only slightly soluble in a mixture of ether and alcohol. Soluble nitrocotton, on the other hand, is practically completely soluble in ether-alcohol and for military purposes the nitrogen content may be from 11.9 to 12.8 per cent.

The nitrocellulose used in the manufacture of army and navy powder is usually referred to by people manufacturing it as "Pyro."

Cotton Purification

The first step in the process of manufacture is the purification of the cotton. The cotton used in this country is either linters or a mixture of linters and the very short fiber remaining on the cotton seed after removing the staple cotton and the linters. The linters and hull fiber, or hull shavings as it is called, as received contain a considerable amount of oily and similar substances, particles of hulls, fragments of leaves, etc. To purify the cotton it is digested for several hours in vertical kiers under pressure. After the cooking cycle is completed the whole charge is blown over into a wash tank where the waste caustic liquor is allowed to drain away and the cotton washed until it is practically free from the waste liquor. The cotton is then transferred to other tanks where the waste liquid is bleached with a very weak solution of bleaching powder and then washed to remove the last traces of bleaching solution.

The purified cotton is run through squeeze rolls to remove a part of the moisture and then passed through a picking machine to open up the fiber. At the time of nitration the cotton should have a moisture content

of not over 1.5 to 2.0 per cent and it is desirable that it be even less than this.

Nitration of Cotton

The cotton is nitrated in a number of different ways but the more modern practice in this country is to nitrate charges of 36 pounds for about 30 minutes in a mechanical agitator, using about 1500 pounds of mixed sulfuric and nitric acids to 36 pounds of cotton. The acid has an initial temperature of 30° to 35° C., but the nitration of the cotton is attended by a small rise in temperature. After the nitration time is completed the nitrocotton is run into a centrifugal wringer which revolves at high speed and is wrung for 3½ to 4 minutes in order to extract as much of the acid as possible. The nitrocotton, containing about a pound of acid for every pound of nitrocellulose, is then dumped into a drowning basin containing a large quantity of cool water and from there pumped to the boiling tubs.

The nitrocotton receives a so-called preliminary boiling treatment in acidulated water for a total of about 40 to 45 hours, which serves to hydrolize and break down the unstable esters, especially the sulfuric esters. After this boiling treatment is completed the nitrocotton is transferred to beating engines, where it is reduced to a finely divided condition by grinding under water. After being ground to the proper consistency the material is run into large poaching tubs provided with stirring apparatus. Here the material receives a total of 12 hours' boiling, divided into several treatments with changes of water in between. After the final boiling treatment the material is given ten cold water washings, being stirred and allowed to settle after each washing. The idea of all this thorough boil-

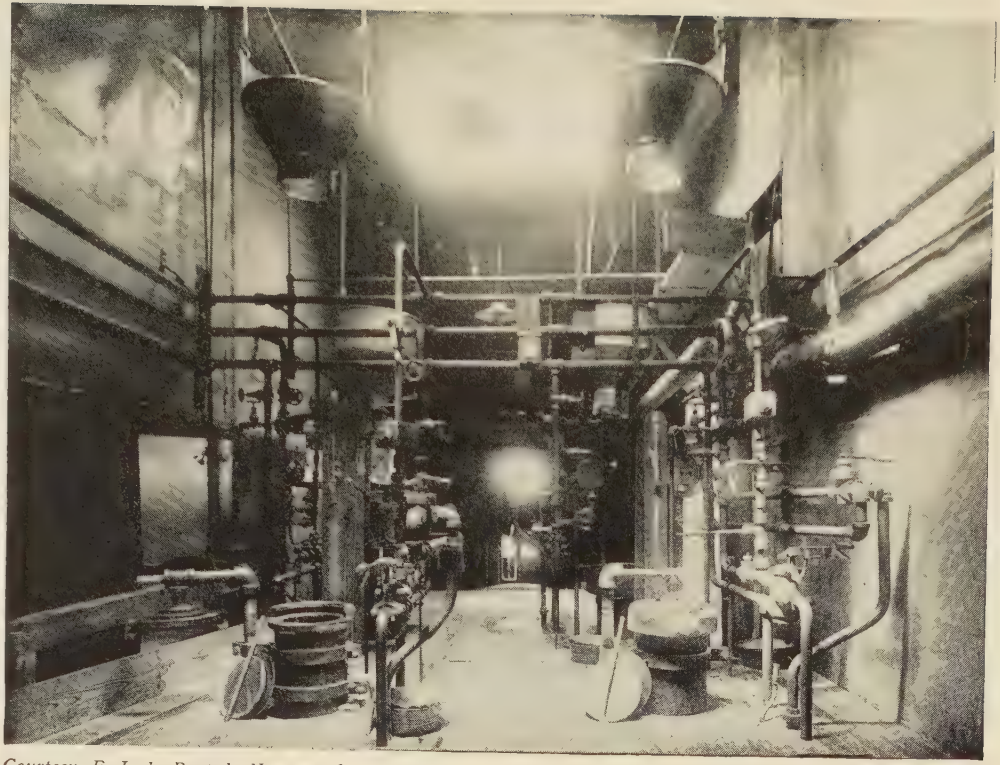
ing, pulping, and washing is to remove all unstable products and traces of acid. The purified Pyro nitrocellulose is finally run into centrifugal wringers which extract from 65 to 70 per cent of the water.

Manufacture of Smokeless Powder

The first process in the manufacture of smokeless powder is the dehydration or removal of the water by means of alcohol.

A charge of wet Pyro with a dry weight of 45 pounds is dumped into a hydraulic press and compressed into a block by means of low pressure of about 250 pounds per square inch. An amount of alcohol slightly in excess of the dry weight of the Pyro is pumped through the block through a perforated screen in the head of the press, and, as it passes down through the Pyro, displaces the water. After all the alcohol is pressed into the block, a higher pressure is applied and the excess of alcohol pressed out, leaving a weight of alcohol equal to one-third the weight of the Pyro.

The blocks of dehydrated Pyro are then sent to a so-called block breaker which consists of a revolving screen of very heavy wire containing balls which break up the block of Pyro into small pieces. The material then goes to the mixing machine which holds about 200 to 225 pounds of Pyro estimated on the dry basis, and sufficient ether is added so that to every 100 pounds of Pyro there are used about 33⅓ pounds of alcohol and 66⅔ pounds of ether. Diphenylamine, which is used as a stabilizer, is previously dissolved in the ether. The mixer is provided with brine refrigeration to prevent loss of solvent. The mixing of the nitrocellulose requires about 30 minutes, at the end of which time a mealy looking colloid is obtained.



Courtesy, E. I. du Pont de Nemours & Co., Inc.

Block Press and Dehydrating House—Smokeless Powder Manufacture.

The colloid is then dumped into a preliminary block-forming press and at a pressure of about 3000 pounds is formed into large cylindrical blocks. Two or three blocks of this size constitute a charge for the finishing press where the colloid is pressed through dies and granulated on cutting machines into grains of various sizes, according to the caliber of gun.

Solvent Recovery and Drying

The powder grains are then transferred to the solvent recovery cars provided with warming coils and condensing coils where they receive a treatment of 4 to 8 days.

Coming from the solvent recovery the powder still contains too great an amount of solvent for use, and this amount depends very largely upon the size of the powder grains, the larger calibers containing the larger amount of solvent.

In order to reduce the amount of solvent to the desired point, the powder is placed in dry houses where it is dried at a temperature not exceeding 55° C. This method of drying, commonly called air drying, usually requires from 50 to 100 days.

Another method of drying very extensively used during the war for the drying of all small and medium caliber powders is the water drying treatment which reduces the time of drying to between 6 and 25 days. In this process powders, after removal from the solvent recovery, are placed in hot water at a temperature of about 55° C. After the powders have been in water for a sufficient length of time to bring the residual solvent to the desired point, the water is drained off and the moisture removed, either by placing directly in an

air dry house or by blowing warm air through and over the powders.

Blending, Packing, and Testing

After the drying treatment is completed the powders are taken to large blending towers in lots of from 100,000 to 125,000 pounds, each lot being given a double blending treatment, in order that each portion of a lot of powder shall be uniform. A definite amount of moisture is left in the powder, depending upon the climate in which the powder is expected to be used. After blending, the powder is packed in zinc-lined boxes, holding about 140 pounds each, hermetically sealed, and kept in this condition until it is made up into charges.

Multi-Perforated Types of Grain

The grains of smokeless powder used by our Government for rifles and certain small caliber cannon are usually in the form of small cylinders with one longitudinal perforation in the center. Such grains are cut from about $\frac{1}{16}$-inch to $\frac{1}{4}$-inch in length. Powder for guns of larger caliber is in the form of cylinders with seven longitudinal perforations—one in the center of the grain and six at the vertices of a hexagon, the perforations being so placed that the six outer perforations will be on a circle, called the pin-circle, drawn with the central hole as the center and having a radius approximately equal to one-fourth the diameter of the grain. Such grains usually have a length of from two to two and one-half times the outer diameter of the grain and the perforations have a diameter approximately one-tenth the diameter of the grain. The dis-

Courtesy, E. I. du Pont de Nemours & Co., Inc.

Rifle Water Dry House—Smokeless Powder Manufacture

tance between the outer edge of the central hole and the inner edge of any one of the other holes, and the distance between the outer edge of any one of the outer holes and the outside of the grain is called the web thickness and it is this web thickness of powder that determines the time of burning of various grains of powder. When a multi-perforated grain is ignited, the grains being very hard and dense, the burning takes place in parallel layers in directions perpendicular to all the ignited surfaces, the outer surface burning with a decreasing surface, while the holes burn with an increasing surface. It can readily be seen then that the time required to consume a grain of powder entirely depends upon the web thickness and it is in this manner that granulations are determined for various caliber of guns. The web thickness for some of the larger guns is as high as approximately 0.166-inch, while the web thickness of powders in multi-perforated grains used for some of the smaller caliber guns is as low as 0.022-inch.

Combustion of Smokeless Powder

The propelling power of smokeless powder in guns is due to the fact that when ignited large amounts of gas are generated as the burning of the grain progresses, and, since these gases are under confinement in the chamber of the gun, a pressure is at once set up, which increases rapidly as the burning progresses and accelerates the burning of the powder. When the pressure of the gases becomes sufficient to overcome the inertia of the projectile in the gun and the resistance due to the friction of the rotating bands of the projectile, then the projectile starts to move down the bore with constantly increasing velocity. In case of

some of the larger caliber guns, the maximum pressure is not obtained until the projectile has moved from 7 to 9 feet.

The advantages obtained by the use of smokeless powder are almost entirely due to the fact that the powder is practically all converted into gas, the principal gases being carbon monoxide, carbon dioxide, and nitrogen, while in the case of black powder, probably not over 50 per cent of the powder is converted into gas. Another great advantage of smokeless powder over black powder is the fact that smokeless powder is comparatively hard and dense and burns only in parallel layers and the burning is under control and is progressive, while in the case of black powder the flame quickly penetrates the entire grain of powder.

In order to obtain proper ballistic results, it is necessary that the entire charge of smokeless powder be ignited as nearly simultaneously as possible, and in order to accomplish this, small charges of black powder are used. Proper ignition of powder is a very important factor in obtaining uniform results. Without proper ignition there is a possibility of hangfires, misfires, and nonuniformity of velocity. The amount and kind of black powder used for ignition varies with the caliber of the gun—from a few grains of fine-grained black powder for the smaller guns to 4 to 5 pounds of coarser grain for the larger guns. In the case of fixed ammunition, the proper charge of smokeless powder is placed directly in the cartridge case, a priming charge of black powder being contained in the primer, which is inserted in the head of the cartridge case. In the case of separate ammunition, the powder is placed in one or more bags, depending on the size of the gun. These bags are made of a special raw silk because it burns up more completely.

Smokeless Powder Used By Great Britain

At the beginning of the World War, Great Britain had Cordite as its standard propellant. Cordite as originally introduced as the British Service propellant in 1889 was of the following composition: nitroglycerine, 58 per cent, guncotton, 37 per cent, and mineral jelly, 5 per cent.

In spite of the cooling effect of the mineral jelly, however, the erosion of the guns was so severe that the composition had to be modified by reducing the percentage of nitroglycerine to 30 per cent and increasing the guncotton to 65 per cent, the amount of mineral jelly being maintained at 5 per cent. The guncotton used for Cordite is of a relatively high nitrogen content of about 13.0 per cent, and is 85 per cent insoluble in ether-alcohol.

Cordite is manufactured as follows: The guncotton is dried to remove moisture and then mixed with nitroglycerine to give a paste. This paste is incorporated in a mixer or kneading machine with acetone for several hours, to form a stiff dough. The vaseline is added during the mixing.

When incorporation is completed the dough is placed in bags and removed to the press house where it is put into gun-metal cylinders, usually being packed tight by a hydraulic ram, and then pressed through a die into cords (hence the name "Cordite") of various sizes, or into tubes. The smaller sizes of Cordite are reeled onto drums as the cords issue from the press, but the larger sizes are laid out on a table and then cut into lengths. Drying is effected in stoves heated to 40° C. and takes two or three months, the time depending on the diameter of the cord. After drying, the Cordite is blended.

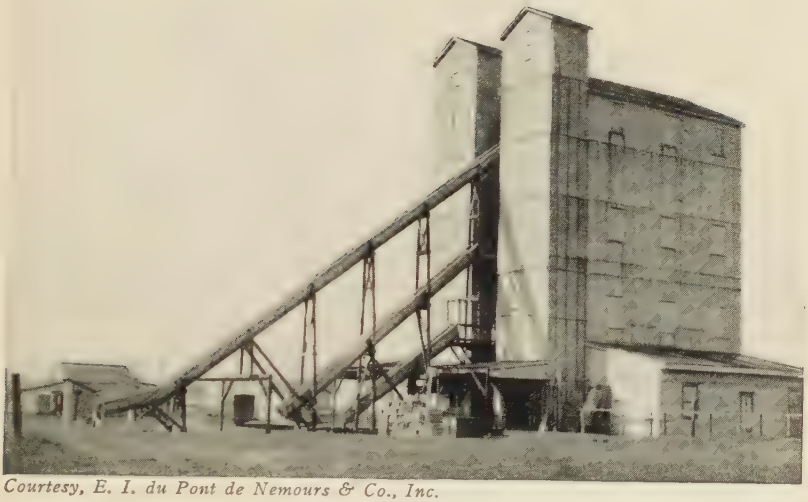
Rifle Powders

As with cannon powders, rifle powders are divided into nitroglycerine and nitrocellulose powders. The powders are made in the shape of small squares or irregular flakes, cylindrical tubes with or without perforations, etc.

The early military rifle powders used by this Government were nitroglycerine powders in several modifications, but on account of the erosiveness of the nitroglycerine powder there was developed in 1909, by the coöperation of experts of the du Pont Company and the Army a nitrocellulose powder made from the same Pyro nitrocellulose as used for cannon powder. The manufacture of this powder is practically identical with the manufacture of cannon powder. The powder is made in small cylindrical granulations with single central perforation. The powder contains 1 per cent of graphite which acts as a cooling agent and as a lubricant, and together with the lower temperature of combustion of the powder, due to elimination of nitroglycerine, materially reduces the erosion. The finished powder is glazed with a small amount of graphite to reduce electrification so the powder will flow readily in automatic cartridge-loading machines. This powder is still the standard small arms powder being used by the United States Government and was loaded in all small arms ammunition used by the Government in the World War.

Wood Pulp Cellulose

The enormous production of explosives caused many times during the war shortages in raw materials and kept us constantly on the alert keeping up our raw



Courtesy, E. I. du Pont de Nemours & Co., Inc.

Blending Tower—Smokeless Powder Manufacture.

material supply. You are all familiar with the fact that due to the blockade Germany ran short of cotton for smokeless powder early in the war and turned to wood pulp as a substitute. This condition of affairs was thought to be impossible in this country, but owing to the severe drought in the summer of 1918 a serious drop in cotton yield from that forecast took place. However, this possibility had been anticipated and for several years the possibility of using wood pulp in place of cotton had been under investigation by an American manufacturer. The experiments showed that using wood pulp alone presented serious mechanical difficulties because of the shortness of the wood pulp fiber. However, it was found that wood pulp could be mixed with cotton to the extent, if necessary, of 40 to 50 per cent, and thus used without inconveniencing the regular factory operations. At the signing of the Armistice arrangements were being made to use a mixture of 75 per cent cotton fiber and 25 per cent wood pulp in the manufacture of smokeless powder.

If the war had continued the United States could have produced, during the year 1919, 1,000,000,000 pounds of smokeless powder. Two-thirds of this would have been available for our overseas forces and the balance would have gone to the allied governments.

Much work is still being done and is to be done in the application of present and future chemical knowledge to the explosives industry in all of its branches—in the improvement of present processes and finished products; in the development of new explosives materials and new processes; in economy of manufacture; and in safety to those engaged in production and handling of explosives. The possibilities are unlimited in this as well as all other chemical fields.

Reading References

Brunswig, H. Explosives. John Wiley & Sons, New York, 1912.

Colver, E. deW. S. High Explosives. D. Van Nostrand Co., New York, 1918.

Escalles, Richard. Explosiv Stoffe. 7 vols. Viet & Co., Leipzig, 1905-1917.

Guttman, Oscar. Manufacture of Explosives; Twenty Years' Progress. Whittaker, 1909.

Heize, F. Sprengstoffe und Zundung de Sprengschusse. J. Springer, Berlin, 1904.

Levy, S. I. Modern Explosives. Sir Isaac Pitman & Son, London, 1920.

Marshall, Arthur. A Short Account of Explosives. P. Blakiston & Son, Philadelphia, 1917.

Marshall, Arthur. Explosives, Their Manufacture, Properties, Tests and History. P. Blakiston & Son, Philadelphia, 1917.

Pictet, Raoul. Zur Mechanischen Theorie der Explosivstoffe. C. Steinert, Weimar, 1902.

CHAPTER X

GLUES AND GELATINS

R. H. Bogue

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Glue and gelatin are not so different, from one point of view, and yet you wouldn't eat a bowl of glue for a box seat at the World Series. It all depends on the way you look at it. Every time Mother boils up a bone for soup, she is making gelatin, and the glue maker makes his glue in the same way. The difference here is one of sanitary surroundings and selection of clean sweet material for the soup, and indifferent surroundings and selection for the glue. Edible gelatin and glue are therefore quite similar except that the former is produced in surroundings that would not offend the most esthetic housewife, and of fresh clean stock, while the glue manufacturer does not conform to this standard of sanitary wholesomeness. Technical gelatin, however, such as is used in photography, is merely a high grade of glue, not necessarily edible, but of specified strength and purity.

Sources

Glues and gelatins are obtained essentially from the skin and tendons and bones of beef and calves. That from calves is devoid of any specific taste and so is most suitable for gelatins that are to be used for mak-

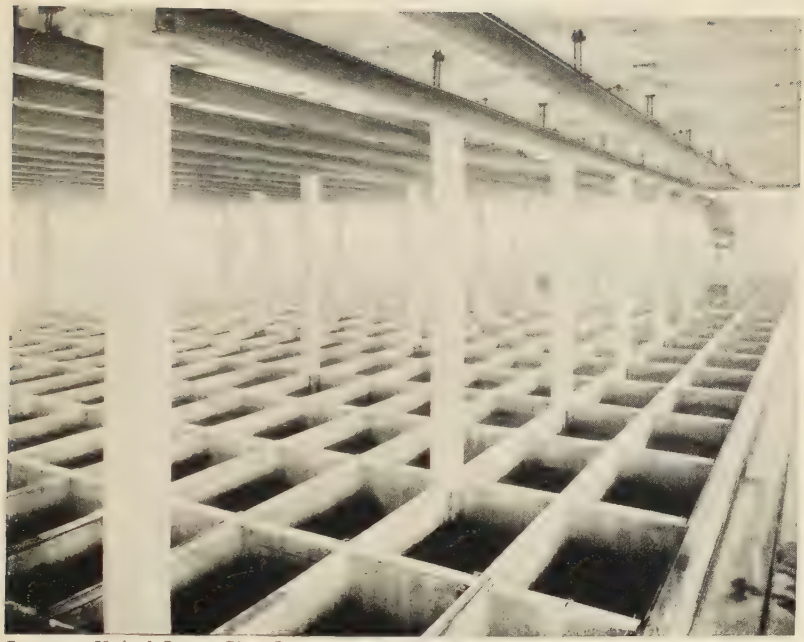
ing desserts where some other flavor is introduced. That from beef gives the strongest product.

The material common to the skin, tendons, and bone, has been found by the chemist to be a protein called "collagen." This is an insoluble material consisting mostly of white fibers of connective tissue. By heating this material in water it is hydrolyzed—that is, it reacts with the water chemically—and forms "gelatin." Bones of course consist largely of mineral matter, as calcium phosphate and calcium carbonate, and the collagen is the organic material upon which the mineral matter is deposited. Sometimes the bones are heated in water directly, but the chemist has found that a higher quality of gelatin may be obtained if the mineral matter is first dissolved in some acid, as hydrochloric. On washing out the acid, the collagen is left in a nearly pure condition, and in this form is called "ossein."

Manufacture

If the skin or tendons or ossein are heated in water directly, they will become hydrolyzed to gelatin only very slowly, and if a high temperature is used, that is, boiling water or steam under pressure, the gelatin produced will not remain as such, but will itself become hydrolyzed to simpler products. These products, which are proteoses, peptones and amino acids, do not have the properties of gelatin. They do not set to jellies on cooling, they are not adhesives (with the possible exception of proteose), and they have a low viscosity. So their presence is not in general desired.

The method most commonly used to avoid this embarrassment is to allow the stock first to swell by soaking in lime water containing a large excess of lime in suspension. A piece of thin limp skin will swell,



Courtesy, United States Glue Co.

Vats in Which Hides and Sinews are Lined

on soaking in lime water for a few weeks, to a thick, rigid, greatly distended slab. When this material is washed to remove the excess of lime and heated in water, it will hydrolyze very readily. A few hours' heating in water at 70° to 80° C. will convert a large portion of the collagen to gelatin, but will be insufficient to cause the gelatin to break down extensively into lower degradation products. This is an old process which was in use long before the chemical nature of the change was understood. However, on studying the reactions the chemist has found that other chemicals besides lime water (calcium hydroxide) will act in a similar manner, though none of them are so well adapted to this use. The swelling he found really due to a particular alkalinity, and this optimum is very close to that of a saturated solution of lime. Now if any readily soluble alkali were used at this optimum alkalinity, or if lime water free of an excess of suspended lime were used, the hide pieces would almost immediately react with the alkali and the solution would then be nearly neutral and require further additions of the alkali to maintain the desired hydroxyl-ion concentration. But when an excess of suspended lime is present, then just as soon as the hide pieces react with the alkali in solution, more of the material will dissolve, so the alkalinity will be held automatically nearly constant. The chemist also found that lime will dissolve mucins and albumin which are present as impurities.

If the liming is continued too long, the stock will dissolve. The proper time for stopping the process is generally determined by noting the feel of the pieces. When properly plumped they are washed and delimed in a dilute solution of hydrochloric, sulfurous, or phosphoric acid. The acid combines chemically with the

lime. Sulfurous acid, in addition to this neutralization of lime, acts as a bleaching agent and as an antiseptic, and so is preferred in glue manufacture, but in edible gelatin its presence is not permitted except in very small amounts.

The stock is usually placed in a large open kettle and covered with water. This is heated by means of steam in coils of pipe along the bottom of the kettle. A few hours' heating at 70° hydrolyzes a part of the collagen. The solution is drawn off and constitutes what is called the first "run" or "boiling". This run produces the highest test glue or gelatin, and each succeeding run gives a lower test product. Succeeding runs are made by adding fresh quantities of water and heating at a somewhat higher temperature for a somewhat longer period. The first runs from a number of kettles are combined for further treatment, and so with each later run, but the several runs are not in general combined. It will be one of the problems of the future chemist to devise continuous extractors, acceptable by the trade, which will produce all of the gelatin in an unhydrolyzed condition. For that which goes to peptones and amino acids is a waste, and the biggest problem of the future in every industry is the elimination of waste.

During the first heating with water, practically all of the fats and greases that are present are melted and rise to the surface. These are skimmed off and by a proper treatment the chemist has refined them to pure white fats which are sold to various trades, depending on the nature of the fat. Much of it goes into the manufacture of soap.

Where a clear product is desired, the glue liquor requires filtration and clarification. Extensive experimentation has shown that best results are obtained

Courtesy, United States Glue Co.

A Section of the Boiling Room Where the Stock is Extracted with Hot Water

by filtering through a loose pulp of cellulose. To produce the sparkling clear gelatins the liquors are further clarified by obtaining a coagulation in them with egg albumin. On heating these solutions, the albumin coagulates and on settling leaves a liquid of remarkable brilliance. These processes of filtration and clarification involve a direct application of colloid chemistry.

The excess of water is commonly removed by evaporation in double-effect vacuum evaporators. Spraying the liquid into a partially evacuated chamber of warm dry air would eliminate many processes in use today, and make a very high quality product, readily soluble. But the market is not yet ready for this type of material. It is for the chemist of tomorrow to effect this change.

When special products are to be made, the required material is ground in at this time. For example, chemistry has shown that if a flexible glue such as is employed for printers' rollers or hectograph plates is wanted, sugar, glycerol, and other ingredients may be added. If to be used in calcimine, zinc oxide, lead carbonate, or calcium carbonate may be ground in. Preservatives may be added at this point, but except when indispensable to prevent putrefaction they should be avoided.

Back in the old days the manner of drying was as follows: The glue liquors were poured into shallow galvanized iron pans, these set in a cool place until a firm jelly was obtained, and the jelly cut by hand with piano wire into slabs which were placed on wire nets. Unfortunately the "old days" still exist in some plants, but this is due, in part at least, to the reluctance on the part of the consumer to use a product different in appearance from that used by his great-

grandfather. The most common practice at present consists in allowing the glue liquors to run onto a wide endless belt which is conveyed slowly through a cooling chamber so that on emerging it is already in the form of a jelly and is automatically transferred to the wire nets. The nets of jelly are placed in alleys or tunnels through which warm air is forced in a direction opposite to that taken by the glue in traversing the tunnels. On emerging, the product is hard and dry and is broken into flakes or pulverized for the trade.

Grading

Glues and technical gelatins are graded and sold primarily on the basis of the firmness or strength of the jellies which are produced in solutions of specified concentration or on the basis of the viscosity of solutions of specified concentration. Certain other factors, however, are of importance in special cases. Thus an excessive foam is objectionable on glues to be used in machine spreaders, while, on the other hand, it is desirable in gelatins that are to be used for making marshmallows. The chemist has introduced many improvements in the method of grading in order that a grade may be a highly significant thing. These investigations are still in progress, and much improvement in method is to be looked for. The federal specifications for edible gelatin require that they shall not contain certain impurities such as copper, zinc, iron, and sulfurous acid in excess of specified maximum values. They also require that the product be manufactured in a sanitary manner from selected stock.

Courtesy, United States Glue Co.

A Part of the Filtering and Evaporating Equipment. Glass-Lined Pipe Lines and Tanks are Used to Avoid Metal Contamination.

Uses

It will probably be a surprise to many that glues and gelatins find uses in such a large number of ways. Most of these are the direct result of chemical research, for the early use was limited to a very few trades. As an adhesive, glue is used extensively in the wood-joining trades and the manufacture of veneers. It is used in making paper boxes and cartons, for book binding, as a leather adhesive, for waterproofing fabrics, canvas, awnings, roofing papers, etc., in making rubber substitutes, and in producing frosted glass. It is used extensively as a size for wall paper, for ordinary sized papers, and coated papers. Glues and gelatins are used extensively in the manufacture of wool, silk, and other fabrics, both as a size to be mixed with the dye, and as a finishing size for the whole. They are used on cotton goods and on cotton batting to stiffen the material. Carpets, tapestries, burlap wall coverings, curtains, etc., are all sized with glues. Straws used in the manufacture of hats are heavily sized. Barrels and casks that are to be used as containers for nonaqueous liquids are commonly sized with glue. A large amount is used in the painter's trade. It is employed both as a size for the treatment of walls prior to the application of paint merely to fill up the pores of the wall, or it may be mixed with a little paint, an insoluble base, and water in the preparation of a calcimine. As a binding agent glue is used in the manufacture of matches, sand and emery papers, abrasive wheels, artificial leather, molding materials, billiard balls, composition cork, and an imitation of hard rubber. As a colloidal gel or jelly glue is used in making printing rollers, hectograph plates, artificial silk, artificial ivory, and gelatin ve-

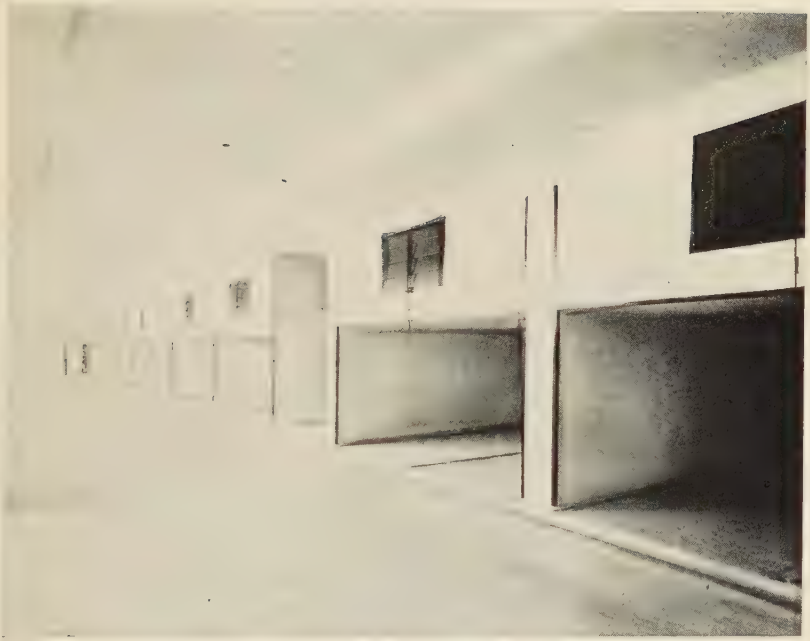
neers. As a protective colloid glue or gelatin has been found to be of great value in electrometallurgical processes, in the manufacture of rubber goods, in acid pickle baths employed for cleaning and removing scale from iron and steel, and in the manufacture of foamite and India ink.

Edible gelatin finds use not only as a food, but as a protective colloid in dietetics and in the manufacture of ice creams and other food products. It is used in the manufacture of emulsion flavors for the baking and confection trades, in making mayonnaise dressing, and has even been suggested for use in the preparation of synthetic milk. It is used in the fining or clarifying of beer, wine, vinegar, etc., and in a number of pharmaceutical preparations, especially for capsules, for coating pills, and for court plasters. Technical gelatin finds its greatest use in photography and photolithography. It is also used as a bacteria culture medium, for making cells for ultra-filtration, for bringing about certain quantitative analytical determinations, and as the medium par excellence for demonstrating a large variety of colloidal phenomena.

Glue as an Adhesive

It obviously will be impossible in the brief space allowed to describe in great detail any of these very extensive uses for glue and gelatin. Only a few uses can be touched upon at all in this place, and these must of necessity be treated with great brevity.

Probably the oldest and most important service for which glue is employed is as an adhesive in the wood-joining industries. Cabinet-making is an ancient craft and still consumes large amounts of glue, and the veneer and panel industries are among the largest con-



Courtesy, United States Glue Co.

Drying Tunnels Through Which Conditioned Air is Forced for Drying Out the Glue or Gelatin

sumers. For all glues that are to be used for joining panels or for other adhesive purposes it would seem that the ultimate criterion for value must be the actual adhesive strength maintained in service. However, research has shown that it is not at all a simple matter to make actual adhesive strength tests which are entirely reliable. In fact, there are some fifteen different factors which have been found positively to affect the results obtainable by such a test. Since it has been found that, in some degree at least, adhesive strength follows the tests previously described for jelly strength and viscosity, these latter are commonly employed to indicate what may be expected in service.

It is surprising how much ignorance still prevails in the glue-handling trades with respect to the proper treatment and application of this product. It is true a great many plant superintendents and glue foremen have initiated in their glue rooms changes which have been in keeping with modern progress, but there are still a great many consumers of glue who are wasting a great deal of money, who are jeopardizing the satisfactory service of the product which goes out under their name, and who are permitting most unsanitary conditions to obtain, all on account of a failure to appreciate the significance of a scientific method in this department. Only a few points of special significance may be referred to here.

Experimentation of the chemist has revealed that there is probably nothing which so damages a glue as heating it in solution for long periods at high temperatures, and yet this is done very commonly and only a few years ago was universal. The writer estimated the loss due to this one cause alone in a single plant which used about four hundred pounds of dry glue per day, as amounting to the sum of fifty-six hun-

dred dollars in a year. This figure, however, represents only the loss in cash value of the glue and does not take into consideration the more important probable failure of their product in service resulting from this practice.

It must also be recognized that glue is an animal product and as such is subject to bacterial decomposition. Such decomposition not only results in a foul smelling and unsanitary product, but also effects hydrolysis and therefore gives rise to a weak material. The Forest Products Laboratory has estimated that the loss in strength and viscosity sustained by maintaining glues at 40° C. for a number of hours is actually greater than that sustained by maintaining them at 60° for the same period. This loss at 40° is unquestionably due to bacterial activities.

Gelatin as a Food

Many people have objected to the use of gelatin as a food on account of the unrefined relation which they think that it bears to glue. It has already been pointed out, however, that although this relationship exists, it should not in any way detract from the dietary use of a properly made gelatin. The role of gelatin in animal economy has been studied by a number of able physiologists and chemists and in the light of their findings there seems to be no question of the value of gelatin in the diet. It does not, however, appear capable of supplying more than about one-third to one-half of the required nitrogenous material necessary to maintain a nitrogen equilibrium in the body. That is, it is not possible to make gelatin the sole source of nitrogen. The reason is believed to be that gelatin is lacking in three important amino acids which are con-

sidered necessary for the building up of protein tissue in the body. In fact, many other pure proteins are also inadequate by themselves, but when mixed with other foods they constitute important sources of nitrogen and of energy. Just as chemistry has revealed the cause of this deficiency, so chemistry at some later time may show how these missing materials may be added, if this should ever be desired.

Gelatin possesses an additional property which is of the greatest value in dietetics, namely, that of a protective colloid. This term has been mentioned before and requires a little explanation. Where two substances mutually interact to form a precipitate or a coagulate it has been found by many investigations that the presence of certain colloidal substances will either prevent this precipitation or considerably modify the rate or nature of it. For example, the casein of milk is coagulated by very small additions of mineral or organic acid. The presence of a very small amount of a protective colloid will make necessary a much greater concentration of acid before coagulation occurs, and the curd will be fine and flaky rather than in the form of a large dense mass. In the milk of all animals there is a protein called lactalbumin which acts as a protective colloid. In woman's milk this is present to the extent of 1.26 per cent against a casein content of 1.03 per cent, while in cow's milk the lactalbumin content is 0.53 per cent against 3.02 per cent casein. Therefore, cow's milk will be coagulated much more readily than woman's milk. For this reason, infants fed on cow's milk are often subject to severe indigestion unless there is added to the milk a sufficient quantity of some other protective colloid to bring the ratio of lactalbumin to casein down to about 1:1 instead of 1:6. Gelatin has been used for this purpose with en-

tire success, and further extensive research on this subject is still in progress. Although this illustration has to do with infant feeding it seems none the less probable that the protective colloid in the adult dietary is of the greatest importance in facilitating healthy digestive processes.

Gelatin is used very extensively in the manufacture of ice cream. A pound of gelatin is used for approximately each fifty gallons of ice cream. This is a small percentage, but amounts to an annual consumption of about five million pounds of gelatin. The advantages obtained by using gelatins in ice cream find explanation in three colloidal properties of the substance: the ability of gelatin to produce a jelly at low temperatures; the protective nature of gelatin, which prevents or greatly diminishes the tendency of other substances to crystallize out; and the ability of gelatin to act as an emulsifying agent and so render more permanent the emulsification of the milk fat in its aqueous medium.

These uses result in an improvement of the body, the texture, and the keeping qualities of the ice cream. If a very rich cream is used there is no necessity for any attempt to improve body or texture, but a large part of the American public demands a cheap ice cream. The introduction of a small amount of gelatin is almost necessary in such ices to prevent the cream from becoming a gruel when a stream of soda water is shot upon it, to prevent little icy spines of water or lactic acid from crystallizing during the first twelve hours, and to prevent it from liquefying by a slightly too high temperature during transportation or handling. Provided a high-grade gelatin is used by the manufacturer, there can be no esthetic objection to its inclusion in ices.

Photography

A large amount of the highest quality of gelatin goes into service as a coating on the film, plates, and developing papers used in photography. Much of the most exhaustive and effectively directed research that has been done on gelatins has been done in the field of photography. In no other department has the chemist made this work so basically the heart of the whole operation.

The coating contains the silver salts and other constituents of the light-sensitive portion of the film. The silver nitrate is precipitated by potassium bromide in the solution of some binding or protective medium. Formerly albumin and collodion were used but now gelatin is almost universally employed. Its function is partly that of a mechanical binder but primarily that of a protective colloid. It functions to diminish the rate of reduction of the silver salts chiefly by a retardation in the rate of aggregation of the reduced silver atoms. During the developing and fixing processes it permits of the ready diffusion of crystalloids, allowing them to be washed out, while it prevents the washing out and the intermixing of the precipitated material. An enormous amount of research is constantly in process in this fascinating field.

Casein Glues

During the Great War it became very important to obtain a glue that would be insoluble and remain sufficiently strong for all purposes when exposed to water or to a highly humid atmosphere. Animal glues were found to be inadequate for this purpose and the United States Shipping Board appointed a committee

to consider the possibilities of casein. The method of manufacture was considerably changed as a result of the investigations of the chemists on this committee. Since another chapter in this book is devoted to casein the detail of preparation will not be given here. It will suffice to say that the committee elaborated a method by which a uniform product was obtained and from it glues of high resistance to water could be made. Since the war, the application of casein for adhesive purposes has increased enormously and it is now largely replacing animal glue both in the veneer industries and in the sizing of papers. It has the advantage over animal glues that it may be mixed in a few minutes and is not retained at an elevated temperature during application. If allowed to remain unused longer than a definite period of time, casein glues will form a jelly which cannot thereafter be applied, but the working life of the average casein glue should be from four to twelve hours. It is necessary that pressure be applied to the joints before permitting the glue to set. This pressure, varying from seventy-five to one hundred pounds per square inch, should remain upon the joints for at least an hour and preferably for a much longer period, as overnight. Following this they should be allowed to condition for a few days before finishing, if the best results are desired. The best strength of these glues is somewhat inferior to that of the best animal glues, but their resistance to water is much greater.

Blood Albumin Glues

Blood albumin glue, like casein, was not used generally before 1918, and was produced for much the same purposes, namely, for resistance to the action of water.

It is commonly prepared from the dried soluble albumin made by coagulating red blood corpuscles and the fibrin, and subjecting the clear serum to evaporation under reduced pressure. The temperature must not be allowed to rise above 160°F., as at that temperature the albumin coagulates. The resulting solid residue is ground and sold as dried soluble blood albumin. As the solubility diminishes with age the albumin should be used for a glue only when reasonably fresh. The glue is made by dissolving the albumin in water and preferably adding ammonium hydroxide and lime. If too much lime is added, however, the glue will set very rapidly to a stiff jelly that is not workable. After applying the glue to a joint the latter must be placed in a hot press or kiln to effect coagulation and hardening.

The water-resistant qualities of blood albumin glue surpass those of casein.

Fish Glue

The most important and abundant of the liquid glues are those made from certain parts of fish. Most of this material is made from the waste products of the cod, haddock, cusk, hake, and pollock industries. The head, skin, and trimmings are all used, but the skins of the cod and cusk are kept separate as the glue made from them is of higher quality than that made from the other stock.

The material is freed from salt, washed, and then heated in water or a dilute acid in much the same manner as has been described for animal glue. Four or five runs of about two hours each are made. Preservatives of phenol, cresol, or boric acid are added. It is then evaporated and some essential oil added to

prevent mold growth and to mask the objectionable fishy odor. The glue is then run directly into the cans or barrels for the trade.

The fish glues of high quality have a gel point of about 7.5°C., and do not contain more than 0.2 per cent of sodium chloride. More salt than this indicates a poor-drying hygroscopic glue which is likely to fail in humid weather.

The best grades of fish-skin glue are used extensively for the making of half-tone plates and to some extent in the production of zinc plates for photoengraving work. These glues also find use where flexible adhesives are required as in bookbinding, and the manufacture of labels, stamps, and court plaster. The advantage of being in a liquid form and available for immediate use gives them priority for all small repair jobs where a strong adhesive is required. Large quantities of fish-head glue are used for sizing, for box making, and in cabinet work.

Other Adhesives

Many other adhesives are in use, but to a much more limited extent than those described above.

The vegetable glues are made usually by the partial hydrolysis of certain starches, as arrow-root, corn, and potato. These may be digested with dilute acids or by enzymes. The product is a heavy viscid material which makes an excellent adhesive for paper and for such articles as do not require exceptionally high strength. Starch pastes are similar, but are made up in the form of pastes to which water must be applied before use.

Proteins extracted from the castor bean have been recommended in England.

Isinglass, which is a form of fish glue, consists of the sounds or air bladders of certain fishes, particularly the sturgeon. These sounds consist almost entirely of collagen and, when brought into solution by heating in water, produce a high grade of gelatin. Its most important use is probably the clarification of wines, beers, and vinegars. It is allowed to swell, then beaten into the wine, for example, and allowed to settle. It is not dissolved, so the fibrous structure has not been lost, and on settling it carries down with it the fine material, yeast cells, etc., which impart cloudiness to the wine.

Some of the vegetable gums as tragacanth, senegal, acacia, and arabic are dissolved or dispersed in water and used in this form under the name of "mucilage." Infusions of linseed, quince seed, and marshmallow root serve a similar purpose. These adhesives are used somewhat for labels, stamps, etc., and for the office, but have little strength.

Many of the algæ and sea mosses have been used for making gelatins and adhesives, but with a few exceptions these applications have been of a purely local character. Irish moss has a particularly pleasing flavor and has been marketed for the home making of gelatins, blanc manges, etc. Agar agar, a sea moss gathered in Japan, is used to some extent in the same manner, and likewise in medicines as a preventive of constipation. It is extensively used in bacterial culture as a medium upon which to produce growth of the organisms.

Sodium silicate, often referred to as "mineral adhesive," is very generally used as the adhesive in the manufacture of fiber board and corrugated papers, and is being employed in increasing amounts in the making of paper boxes and cartons. It sets very

rapidly and is sufficiently strong for the purposes mentioned.

Conclusion

The account which has been set forth is brief and fragmentary. From it some idea may be gained of the nature, the sources, the manufacture, and the uses of glues and gelatins. For those who wish to pursue the subject at greater length, there is appended below a select bibliography.

The industry is as old as human records allow us to extend an inquiry. But the progress of recent years is the result of patient investigation by the chemist. He has changed rule-of-thumb methods in manufacture to control based on an intelligent application of scientific principles. By an understanding of the colloidal behavior of these materials, he has extended their uses to fields in which these properties become of the utmost importance and significance. Their function and value in animal metabolism has been established.

These studies, however, are young, and research in many of the most significant departments still awaits conclusive solution. This may not be accomplished in a year, but will require many years of study by many able investigators.

But the greatest lure of research lies in those realms of ideas that are not yet born, but which become crystallized in the mind of the investigator only with the years. To find the greatest light implies close application, diligent study, a fertile imagination, a keen intellect, and a oneness of purpose. These together are capable of bringing to fruition the flimsy things of which dreams are made.

Reading References

Adhesive Research Committee. First Report. Department of Scientific and Industrial Research, London, 1922.

Alexander, J. Glue and Gelatin. Chemical Catalog Co., Inc., New York, 1923.

Bogue, R. H. Chemistry and Technology of Gelatin and Glue. McGraw-Hill Book Co., New York, 1922.

Bogue, R. H. The Theory and Application of Colloidal Behavior. McGraw-Hill Book Co., New York, 1924.

Loeb, J. Proteins and the Theory of Colloidal Behavior. McGraw-Hill Book Co., New York, 2nd ed., 1925.

Sheppard, S. E. Gelatin in Photography. D. Van Nostrand Co., New York, 1923.

Thiele, L. Leim und Gelatine. Leipzig, 1923.

Tressler, D. K. Marine Products of Commerce. Chemical Catalog Co., Inc., New York, 1923.

Wilson, J. A. The Chemistry of Leather Manufacture. Chemical Catalog Co., Inc., New York, 1923.

CHAPTER XI

THE CHEMISTRY OF INKS

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No sooner had the state of civilization developed to the point where it became desirable to make temporary or permanent records than man found his clay tablets and carvings on stone absolutely inadequate for the purpose. The invention of the papyrus roll and sheet necessitated also the invention of fluid and semifluid inks capable of being used thereon, first by the brush and later by the pen. Old papyri dating back to 2500 B. C. were written upon with black ink which was an infusion of lampblack and glue with a preservative to prevent decomposition.

It is an interesting fact that today the draftsman, the artist, and the architect use carbon inks made by a formula very much like the ancient one of mixing fish glue with lampblack obtained from burning pine wood, and for their purposes, no other equally good ink has been found. This type of ink is still used to a large extent for all purposes in China and Japan, and to a lesser extent in other Asiatic countries. Searches through old manuscripts from practically all the civilized world seem to prove that nothing better had been discovered down to the tenth century A. D. It is well that such was the case, for the absolute

permanence of the carbon inks can be approached by few other substances.

Oxides of iron and other minerals might have been used, but over long periods of time they apparently had a destructive effect upon the fiber, while the carbon inks actually seem to have assisted in the preservation of the surface upon which they were deposited.

It is not known who discovered the iron tannin and iron gallotannate inks, but on account of their ease of preparation, highly fluid character, and better working qualities, they came into use quite universally about the tenth century A. D. Records made with these inks after that time are often much more poorly preserved, and their legibility has suffered to such an extent that in certain instances, because of the character of the ink used, they have become almost valueless.

There are many formulas for making the iron gall inks, almost any of which will yield a black or blue-black. Practically all of them consist of indefinite mixtures of the tannates, gallates, and gallotannates of iron made by mixing solutions of iron sulfate or iron vitriol with extracts of gallnuts from various trees. It may be said that, except for improvement in quality, many of our writing fluids today are similar in chemical composition to those which have been used for almost a thousand years. Needless to say, the chemist has added vastly to the quality of the products by controlling the composition and the determination of the chemical structure of the tannic and gallic acid salts of iron, and, in general, has brought the iron gall inks to a high state of efficiency, although they are still unsatisfactory from the standpoint of permanency and do not begin to compare with the permanency of the inks made from a suspension of carbon.

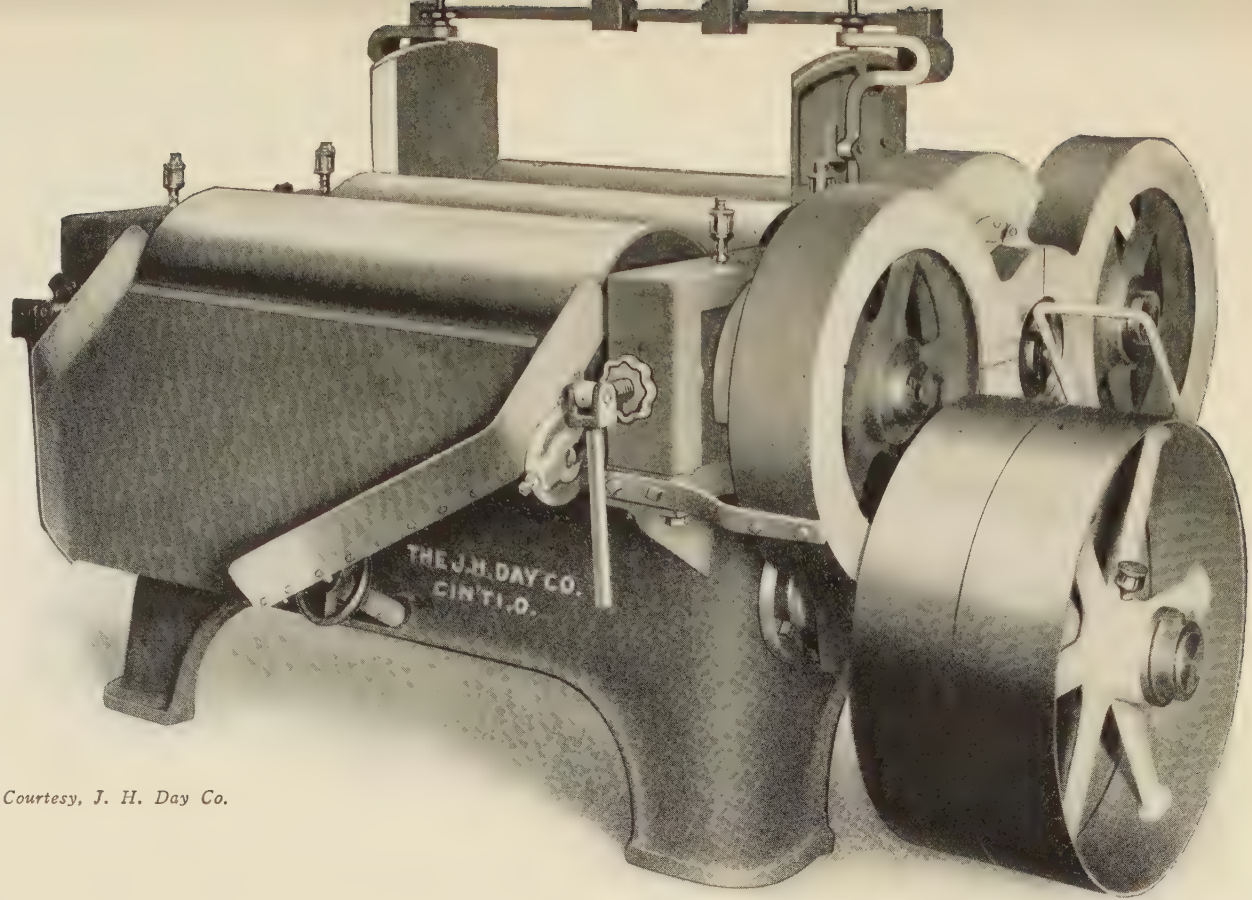
Colored Inks

The first use of colored inks dates back to the time of Plutarch. We find that the ancients used colored extracts of plants and pigments, from any source whatsoever, which they mixed with glue or gum solutions. Their lack of more suitable substances is shown in their laborious and painstaking efforts at ornamentation in many of the old manuscripts where the letters were cut from gold leaf or foil and then made to adhere to the surface by means of none too permanent adhesives.

Coal-tar dyes added vastly to the writing-fluid field, giving a variety of colors hitherto totally unknown. The chemist, in searching for dyestuffs suitable for textiles, made many which were entirely unsuited for fabric, but a few were highly soluble, of a fair degree of permanency, and satisfactory for writing fluids. In spite of their low cost and high color value, they have not replaced sepia, from the ink sac of the cuttle-fish, and sepia inks are still used by the artist, regardless of their cost.

Logwood yields another natural extract which has been used for a long period, but which has been vastly improved by the work of the chemist in isolating the pure hematin and hematoxylin. The chemist has also added chromium and vanadium salts to the iron gall inks with beneficial effects so far as permanency is concerned.

In the colored writing fluids today, the coal-tar dyes are used almost exclusively; thus, naphthol yellow, metanil yellow, and tartrazin for yellow; orange 2 for orange; eosin and rhodamine for red and blue-red; fuchsin and methyl violets for the reddish violet and true violet shades; and alkali blues, derived from



Courtesy, J. H. Day Co.

Ink Mill

fuchsin, for very bright shades of blue. Blues are also made by dissolving Prussian blue, a cyanide of iron, in oxalic acid. Many other dyes are used for special shades.

Some inks are made by compounding various coal-tar dyes with the iron gall inks as a base, principally in order to prevent fraud, such as the raising of paper money and bank checks and the falsification of documents. The most common erasing fluids used consist of an alkali hypochlorite which is first applied to the ink to be removed, followed by an application of dilute acid. The liberated hypochlorous acid exerts a powerful oxidizing effect upon the ink, either completely bleaching it or rendering it soluble so that it may be easily washed out. Attempts to prevent such frauds have to a considerable measure been successful, due to the composition of the inks used, for some of them which contain two ingredients are not completely bleached, with the result that attempted erasure simply changes the color. Certain types of black inks will turn blue and remain blue under the action of the bleaching agent.

Printing Inks

Largely on account of the comparatively limited scope of the writing-fluid field and its problems, the advances have been nothing to compare with those made in the field of printing inks, where the problems are infinitely broader and more intricate. Since the invention of the printing press, credited to Gutenberg in the fifteenth century, probably no industry has shown a development in more numerous fields and along broader lines than has the printing art. Old Chinese records dating back to 1200 B. C. mention printing from engraved

characters, and in 927 A. D. tell of printing from stone and blocks for the Imperial College at Pekin. This was all no doubt hand printing, and not until the invention of the printing press was there any material advancement in the art. We may say, therefore, that from 1000 B. C. to 1500 A. D., twenty-five hundred years, the printing art was practically dormant. The invention of the press necessitated immediate and rapid improvements in the manufacture of inks, and as the styles of paper and presses changed and the speed and number of surfaces upon which it was desired to print increased, the ink makers' problems multiplied many fold.

Forms of Printing

Printing may be divided into three distinct classes, the first of which is that from engraved surfaces. An engraving is made upon metal or other surface and the ink is then rubbed over this surface to fill the depressions. When the paper comes in contact with the surface, it lifts the ink from the depressions, leaving the flat unengraved surface clean. Our fine etchings and paper money are examples of the finer art of this type. The Sunday supplements of many of our newspapers, usually brown in color, are printed by a very rapid process from engraved rollers (intaglio process).

Second is the printing from flat surfaces, as in the lithographic process. The principle of this process depends upon the fact that when a design is drawn upon a smooth stone of a certain type with a grease pencil, lithographic inks will adhere to the design but not to the remaining area of the stone, provided it is kept moist. The paper lifts the ink deposited upon

the design drawn with the grease pencil. This is the lithographic process in its crudest form. Its higher development has been due to the discovery of processes for rapidly transferring intricate and highly complicated designs to the printing stones, and also to the discovery that an etched zinc plate can be used in a similar manner. Advertising posters, illustrations for fine books, and numerous other examples might be cited where this process of printing is used exclusively. Stock and bond certificates are mainly lithographed.

The third type of printing is that from raised surfaces, such as the ordinary type commonly used in every newspaper office.

Properties and Composition of Printing Inks

Now, it is obvious that the properties of inks for each purpose must be different and each one must be specially prepared. In printing with type from the newspaper press at very high speed, the drying is principally by absorption and the inks consist largely of carbon black and lampblack ground in a mineral oil. The better grades of such ink contain small amounts of drying oils and possibly a drier. Also, because most black pigments such as lampblack are not truly black, but brown, a so-called "toner" is added to the ink to offset the brown shade. These toners are usually oil-soluble dyestuffs, such as induline and methyl violet base.

In lithographic printing, the drying is mostly by oxidation of the drying oils and varnishes of which the ink vehicle consists. The pigments are ground into varnishes, which must not be affected by water; neither must the pigments be in any measure water-soluble,

since the colors would bleed out onto the wet portion of the plate or stone and eventually stain the paper with which they come in contact.

The character of ink for printing from depressed surfaces depends upon the kind of plate and speed of operation; thus, hand printing of fine engravings requires an ink which will dry by oxidation, but it must be of a short or "buttery" character, so that it will readily lift from the depressions. In the intaglio process, where the printing is done from engraved copper rollers at very high speeds and the drying is mainly by absorption, the pigments must be very light in character, thoroughly suspended in a highly fluid vehicle containing little or no drying oil and usually no drier.

Another property of vital importance to the printer using colors is the opacity or transparency of the inks. We are all familiar with the beautiful reproductions of some of our finest paintings, made by what is known as the "three-color process." Practically the entire range of the color spectrum can be obtained by the artist by mixing yellow, red, and blue, and the printer in a similar way obtains his beautiful color effects by the use of three colored inks and a black. Such printing is usually done from etched copper plates, using one plate for each color, and it is obvious that the three or four plates used must be in perfect register in order to deposit their particular color in the right place, for even the faintest hair line out of register will usually ruin a fine picture. If the yellow be printed first, and the red, blue, and black in order, the color of each layer of ink must show through the others to give a perfect blend, and therefore the top layers of ink must have a high degree of transparency. Even the underlying coat of yellow must be a trans-

parent product to give a properly blended series of inks which will reproduce a perfect picture. This problem of the transparency of inks is dependent upon two factors: the color of the varnish, which should be nearly water-white (but never is), and the transparency of the pigments. Most of us think of pigments as practically opaque, while, as a matter of fact, some are so transparent that when rubbed up in oil or varnish and spread in a thin film on glass, they scarcely alter the transparency of the varnish itself. Highly transparent white pigments of this type are alumina hydrate and magnesium carbonate. In order of transparency, others most commonly used are zinc oxide, blanc fixe (precipitated barium sulfate), and titanium oxide, the latter being exceedingly opaque. In fact, it is the most opaque white pigment known, even thin films of it almost completely stopping the passage of light. Several other white pigments that are used to a more limited extent for such purposes have varying degrees of transparency.

Lake Colors and Pigments

In color printing, only the finest and most permanent lake colors are used. By "lake colors," we mean the insoluble salts of organic dyestuffs. Of the many thousands of coal-tar dyes discovered, only a few are suitable for making lakes, because their mineral salts are soluble in water, and when ground into ink varnishes, give inks which will bleed when wet with water. A good dyestuff suitable for lake making, when dissolved in water and treated with a suitable portion of a mineral salt, such as barium chloride or lead acetate, will yield a precipitate which is totally insoluble in water, and if the dyestuff be pure, the re-

sulting pigment settles out of the solution, leaving the water layer clear. Such lake pigments are made from acid dyestuffs, not only as their lead and barium salts, but occasionally as their calcium and strontium salts, and it is remarkable that the shade of color obtained by use of the different metals with the same dyestuffs varies vastly. The lead salts are usually the lightest in shade, the barium appreciably darker, and the calcium the darkest of all. The transparency of the three also varies appreciably.

Basic dyestuffs, since they contain no acid group and cannot yield lakes by forming a salt, are precipitated in the form of lakes by means of tannin and tartar emetic, or with such well-known precipitating agents as phosphomolybdic and phosphotungstic acids. Lakes of this series, as a general rule, possess great brilliancy. There are other types of organic coloring matters which are not lakes but simply insoluble dyestuffs which possess a high degree of opacity and are used for special purposes.

Ink Driers

A very essential feature of a printing ink is its rate and mode of drying. Only when the paper to be printed upon is unsized and possesses a high degree of absorptive power can the inks be depended upon to dry by absorption. Our fine printing is nearly all done on sized and often on supercalendered paper stock, and the inks must dry by oxidation. Now, since the usual drying oils take many hours to set without the aid of a catalyst, organic salts of lead, cobalt, and manganese in the form of their resinates or linoleates are added to the inks and speed up the drying remarkably. They function, however, in different man-

ners. Cobalt causes the ink to dry rapidly on the surface, giving a thin skin with the soft ink underneath. Lead and manganese dry more uniformly throughout the body of the ink, but do not possess sufficient speed. As a general rule, we may say that the best ink driers consist of mixtures of the three, and that such mixtures will cause the ink to dry uniformly throughout the thickness of the layer within a reasonable period of time.

Printing Surfaces and the Ink Makers' Problems

When we consider the numerous types of surfaces upon which inks must be used, we can readily appreciate some of the problems encountered by the ink maker. The following list of printing surfaces will give some idea of the extent of the ink makers' problems: newspaper stock; bond and book paper; label stock; bread wrappers; food cartons; soap wrappers; wax and glassine papers; sign and poster stock; paper bag stock; cloth bag stock; sheet metal; tin foil; cellophane, and celluloid. In addition to these, the ink maker is called upon to make inks for typewriter ribbons, stamp pads, check protectors, laundry marking, and gold and silver inks for many purposes. The properties of the inks for each of these purposes and many more are distinctly separate from each other, and each printing surface presents its individual ink problem. Thus, the ink on a typewriter ribbon must not dry on the ribbon but must dry quickly on the paper. The same is true of the stamp pad and check protector. The ink for bread wrappers must be nontoxic and the pigments used must be totally oil-insoluble. The ink for soap wrappers must be absolutely fast to alkali and nonbleeding in oil, as otherwise the

printed design on the paper will be quickly transferred to the soap, a very objectionable feature.

Some of the printing presses work at great speed over paper drawn from rolls. The printing is done from plates on a cylinder and several cylinders may be on the same press, where two or more colors are printed at the same time, so that there is practically no time allowed for one coat of ink to dry before the second coat is applied. In this case, the problem must be met by making inks of different body, the first coat possessing the heaviest body, the second a lighter body and the third still lighter. By the "body" of an ink, we mean its rate of flow, its tack (stickiness), or its viscosity. The term "body" implies many specific properties within itself, for an ink may be thick and yet be "short" like butter or "long" like varnish, and the tack must be very carefully adjusted for use on different presses. It is obvious that a press running at the rate of one thousand impressions per hour would take a heavy-bodied ink with appreciable tack and still permit the paper to be drawn from the plate without tearing, while should the same ink be run on a press at a rate of many more thousands per hour, the tack of the ink would be so great as to cause the paper to tear when the press removed the sheet from the type or plate.

Adjustment of tack and viscosity is done by altering the composition of the varnishes and other vehicles, and this brings up the question of the varieties and kinds of varnishes. For ordinary printing, where the inks are allowed to dry by oxidation from the air, linseed varnishes are largely used. In order to adjust the tack and viscosity of the inks, varnishes varying greatly in body are used, the thinner ones being almost as thin as the oil itself, the heavier ones so heavy

that they will no longer flow. Soy bean and China wood oils are used as well as linseed, and for black varnishes asphalt is dissolved in the oils. Rosin oils, petroleum, and rosin varnish are also common vehicles.

From the above, it is evident that many of the problems of the ink maker are purely physical, but by far the major portion are purely chemical problems, for the drying of the inks, the composition of the pigments, the body of the varnishes, and their composition must be governed chemically. The acidity of the ink varnishes is a vital point for certain inks, and the small acid content must be neutralized with lime or other alkalies.

Press Room Problems

Even after the actual preparation of the inks in the grinding rooms, the ink chemist has his troubles in the press room. It is often impossible to predict what troubles may be encountered, owing to the wide variety of presses, the numerous kinds of papers and paper sizings, the speed of the press, and the personal equation introduced by the variation in methods of operation by different printers. There may be trouble with the ink drying on the rollers. It may creep or crawl on the rollers much as we have seen a poor varnish creep, crawl, or check on a piece of furniture. It may not dry to a homogeneous film, or the film may be lacking in gloss when dry, or the gloss may be too high. Pigments of certain types tend to float on the surface of the ink film after it is printed, giving a chalky effect to the print, and other types of pigments may sink in the film, giving the appearance of a great excess of varnish. Too highly acid ink varnishes may cause the finished ink to "take on water" and emulsify with it; the ink may fail to "lift" properly from the

type or stone, or it may "pile" or "build up" on the type or plates, necessitating the complete stopping of the presses so that the plates can be cleaned; it may fail to take a quick "initial set," and great piles of the printed sheets then stick together when stacked as they come from the presses; or the ink may "offset," the ink on the freshly printed sheet staining the back of the next sheet coming on top of it from the press. There are other problems too numerous to mention.

Many pigments are known to have what is called "bronze." Ink made from such pigments, printed on white paper, when dry will show an entirely different color by reflected light when looked at from different angles. Some pigments show the marked beetle-green effect of the coal-tar dyes in crystalline form. Sometimes the bronze is desired, as in the printing of labels and posters, and at other times it is not, as in the printing of pictures, and the accurate control of the bronze effect is still puzzling the ink chemist. We often know how, but not why, an effect can be obtained, and the multiplicity of factors involved in this control of the bronze effect is so great that a long period of time will no doubt elapse before it can be felt that perfect control is to be had through our knowledge of chemical and physical laws.

Extent of the Industry

Some idea of the vast extent of the printing ink industry may be gained from the fact that it is estimated that ten million dollars' worth of ink is used annually on Manhattan Island alone, and the total consumption in the country, taking in all classes of inks, probably amounts to one hundred million dollars per year. It is as great as our dye industry,

about which so much has been written, and is far greater than the business in perfumes and essential oils. While the major portion of all the inks in pounds is black, much the larger portion in cost is colored, for the cheaper black inks for newspaper printing cost only a few cents per pound, while the finer colored inks for process printing may cost several dollars per pound.

Someone has said that "the state of a nation's civilization may be judged by the amount of soap which it consumes." It would seem that we might judge it even more accurately from the tonnage of printers' ink used annually in recording its accumulated knowledge.

CHAPTER XII

LUBRICANTS

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Lubrication is quite the most important factor in the operation and maintenance of every form of mechanically operated appliance. Without lubrication, machinery as built today cannot be operated, and with poor or insufficient lubrication, the equipment cannot be maintained in service for very long.

The purpose of lubrication is to keep rolling or sliding surfaces apart. Under a powerful microscope the finest bearing surface in the best made machine will appear to be made up of hills and valleys. A cross section will look like a saw. Should two such surfaces be required to move upon each other while dry, the hills will be mowed down, and this constitutes wear. Should the operation continue, heating will occur. Finally, if these surfaces are parts of a machine, heating will expand the metal and the surfaces will seize, effectively stopping the motion, if not entirely ruining the bearing.

SELECTION OF PROPER LUBRICANT

Any lubricant such as water, oil or grease, graphite, or soapstone, placed between the moving surfaces fills up the "valleys" and keeps the tops of the "hills" from striking, until the amount of lubricant is reduced,

by leakage, to a point where the "high spots" strike. Although the resulting wear may not be enough to cause trouble, the lubricant will be found to have taken up a certain amount of metal which may have no more detrimental effect than to color the lubricant black.

Should the lubricant be too thin, and not have body enough for the work to be done, the film between the surfaces is not thick enough to keep the high spots from coming together and wear progresses very fast. Also thin oil will easily leak out and away from the surfaces to be lubricated.

A very thick lubricant will keep the surfaces apart and prevent striking of even the highest spots, while the heavy nature of the lubricant will prevent its leaking and will make it last for long periods. If reducing wear and the amount of lubricant used was all that was required, it would only be necessary to use the heaviest bodied oils or greases obtainable.

Friction, however, is just as important a factor as wear. Lubricants are made of various consistencies having various thicknesses of film or different bodies, the heaviest causing the greatest fluid friction and the thinnest giving the least. It takes less power to operate a machine with a thin lubricant unless the lubricant is too thin, but of course, it takes more power to wear out bearings than to turn them when properly lubricated. If the heaviest known lubricant were to be used between two moving surfaces, the surfaces would not touch and therefore would not wear, but the lubricant would act as a brake. This would be due to the fact that that part of the lubricant nearest to the metal would cling to that surface, and all of the parts of the lubricant in between would cling to each other, effectively holding back the motion of the mov-

ing surface. This is called fluid friction and is covered by the laws of hydraulics. It may be compared to the effect of a boat going through the water, giving motion to various strata of waves or films of water. The film next the boat travels at about the speed of the boat and every succeeding film or layer of water travels at a slower speed, until the outside layer has but little motion, being next to still water. This holding back or resistance effect of the films of water is very great as the speed of the boat increases, and varies as the cube of the speed.

There is, therefore, an art or science of the application of lubricants; some machinery must be lubricated with very heavy oils or greases, whereas other machinery cannot operate except with the thinnest of the oils.

Whether a machine shall have applied to it a heavy or a light, a thick or a thin lubricant, depends largely upon the equipment for supplying the lubricant, and this brings in another factor which has much to do with successful lubrication.

The history of the development of all steam engines, steam turbines, gas engines, and machinery in general is closely related to the evolution of the lubricants and their application. At the time of the discovery of petroleum, the development of high-speed machinery had about reached the working limit of the animal and vegetable fats and oils which were the only available lubricants and further mechanical development was possible only with the mineral oils.

In the early days the methods employed for producing the various lubricants were as crude as the general methods used for making the machinery upon which the oils were used. Everything was in a primitive state.

All animal and vegetable oils are subject to gradual

oxidization which produces free fatty acids and gums. The acids attack the metal. The gums offer resistance to motion and also stop up oil passages, preventing the oil from reaching the bearings, which causes heating and burned out bearings.

The improvement of machinery forced an improvement in lubrication, either through better methods of application, or through an improvement in the lubricant itself. Throughout this development the engineer has always worked with the chemist, one in the field of application and the other in the laboratory and refinery. Their combined efforts have greatly assisted the present development of machinery, and they are still working on the practical problems due to the conditions under which our modern machinery must operate.

Historical

James Watt's improvements in relation to the steam engine during the last of the eighteenth century revolutionized manufacturing and made possible our present industrial era. The first attempts to harness power and to do work by machinery were necessarily crude from all of our present standards of engineering, metallurgy, industrial chemistry, production, and lubrication.

The earliest lubricants were oils and fats extracted from animal and vegetable matter.

In the first power-driven manufacturing plants with the earliest forms of steam engine, beef tallow was the lubricant used for all heavy work. Tallow was melted in a tea pot set on the steam chest, and the tallow oil was occasionally put into the steam chest by means of a small hand pump. Hard tallow was packed in the

heavier bearings and was mixed with red lead to lubricate the gears.

Sperm oil, taken from the head of the sperm whale, was the approved lubricant for spindles, looms, and all lighter machinery, and was also used in the lamps and torches for illumination. Sperm was easily saponified and was used as a filler for shoddy wool so the fiber would cling while spinning. It was also very fine for dressing leather belts and leather aprons used to cover certain revolving parts of the production machines.

The popular and authorized combination for total lubrication in the early machine shops was beef tallow, castor oil, and lard oil. Lard oil could be used as a lubricant, a burning oil, for belt dressing, and also on the cutting tools for iron or steel.

Olive oil and coconut oil had many uses, and the fact that they were edible introduced many interesting complications. Olive oil was used as a general lubricant for light machinery, as a burning oil, for emulsions used for mixing with short wool fibers, and for dressing leather. It was also used by the mill hands for salad oil and for frying food.

Methods of Applying Lubricants

With the primitive forms of machinery the lubricant is always applied by hand, the oil being used but once. This method is also referred to as intermittent lubrication because there is, first, a flood of lubricant, which gradually wears off until the bearing may become quite dry before the next flood. With this form of application the gum-forming and sticky nature of the animal and vegetable oils is not as detrimental as one would suppose. There is, however, a considerable risk of heating and seizing the bearing.

However, the effect of the gums and acids of these organic oils began to be seen when the first improvements of application were made. When cup oilers or bath bearings were introduced in an attempt to secure more continuous lubrication, the animal and vegetable oils were found to leave serious deposits. Continuous use of the same amount of lubricant was found to be impracticable since the oil gradually thickened and the deposits and sludge stopped the circulation. The limit of machine development and of the lubricants available had about been reached.

All conditions for the birth of modern industry were forming during the early part of the nineteenth century. The French chemist, Eugene Chevreul, in 1813 discovered the true composition of animal and vegetable fatty matter. He found that the naturally occurring fats and oils were chemically composed of an acid and a base, and belonged in a definite class of chemical compounds.

The attention of chemists was attracted by this work with the net result that better refining methods were introduced. The early development of the lubrication of machinery, therefore, had the assistance of the chemist in a better preparation of the only available lubricants—fats and oils.

The demand for better lubricants increased with the general acceptance of machinery, and with the need of keeping the machinery in repair and in motion.

Previous to 1870, it had become apparent that some study should be made of lubrication and the Institution of Mechanical Engineers of England appointed a lubrication committee headed by Beauchamp Tower, whose report was published in the 1883 Transactions of the Society. He found that bath lubrication would give the safest lubrication and require the lowest oper-

ating power, compared to hand oiling, where oil was applied by means of an oil can at irregular intervals with its attendant risk of heating and seizing of the bearing. The report also established the fact that different methods of applying the same lubricant gave widely different power requirements in operating a machine, and that loads could be greatly increased without burning out the bearings if the best methods of application were employed.

The foregoing research work established the following steps or stages in the method of lubrication.

THE EVOLUTION OF THE METHOD OF APPLYING LUBRICANTS

No. 1, Primitive. Hand oiling, the oil being applied with an ordinary oil can, from which the oil is applied at irregular intervals. The poorest results are chargeable to this method of lubrication.

No. 2, Siphon, or Drop Feed Oilers. Slightly better results are obtained with this method of application, as the supply of oil to the bearing surface is delivered in small amounts at regular intervals.

No. 3, Pad Lubrication. This is an improvement over No. 2 as there is a constant flow by capillary attraction of lubricant to the bearing surface. The pad, especially in railway axle lubrication, applies the lubricant to the under side of the axle and away from the point of greatest pressure, which is always desirable.

No. 4, Bath Lubrication. The best results are obtained by this method of flooding the bearing surface with oil, only one-tenth the power being required to move a bearing under this form of lubrication as compared with the primitive method of hand oiling.

This was the state of knowledge in 1880 when the American mineral oils from Pennsylvania were being first developed.

At this critical period in machinery development, mineral lubricants were introduced. Considerable difficulty was encountered in their introduction, due to the peculiar fact that a bearing once lubricated with animal or vegetable oil will absorb the free fatty acid thrown off by the oil. When a mineral oil is put on the bearing, a physicking effect is produced which generally results in a hot bearing. This is because the

mineral oils remove the gums from the pores of the metal. These gums in some cases roll up like soft varnish and fill the oil ways and oil holes, thus effectively preventing lubrication.

It was discovered that damage could be prevented by gradually mixing the mineral oils with the animal or vegetable oils. A gradual absorption of the gums occurred, thus making the transition from one oil to the other without difficulty.

Troubles of a psychological nature were also encountered. The engineers on the Rhine tow boats would not approve of American mineral oil for the engines after one attempt to fry fish in the American product. Mill operators in Italy did not like salad dressings made of Pennsylvania neutrals. Mill hands in Bombay likewise objected to the peculiar taste of Bayonne spindle oil and reverted to the much liked coconut oil. All of this required much ingenuity on the part of the American refiners' representatives in making the turnover.

Finally the mineral oils were successfully established, with a considerable improvement in the general mechanical efficiency of machines and a materially lowered cost of lubrication. This period saw the gradual extension of the mineral oil business in lubrication and illumination and the gradual cessation of the use of animal and vegetable oils for these purposes. Then came two further stages of lubrication improvement that brought the art of applying oils up to its present high state of development.

No. 5, Gravity Feed Lubrication, where the oil is pumped to an overhead tank, from which it flows by gravity to the bearings to be lubricated. This is flood or bath lubrication, with the addition of pressure from height of oil above the bearing.

No. 6, Forced Feed Lubrication, where the oil is forced to the bearing by pressure pumps. The pressures can be regulated to any point desired to assure complete flooding of the bearing surfaces.

Refinements have been added to these last methods of application in the form of settling tanks, filters, separators, heaters, and coolers that bring the application and care of oil to the highest engineering level.

Improvements in Petroleum Lubricants

With the improvements in machinery and in the art of application, marked improvements in the methods of producing oils have naturally followed, and most of the credit for these improvements must be given to the chemist, either for his direct work or for his assistance on the important problems.

In the petroleum industry the first chemical laboratory instruments used were mainly for the purpose of controlling the manufacture of petroleum burning oils. Later on many of these same instruments were used in the refinery to standardize the various kinds of lubricating oils. In this manner certain characteristics of the lubricant were used, first, in controlling manufacture, and later in classifying the finished product for sale and application. The first mineral lubricants were made from Pennsylvania crudes. The gravity of each cut was different and as long as the same crude was used as a base, gravity could be used to classify the various products: 34° gravity Baumé oil would be a light spindle oil, 28° gravity oil would be a medium spindle oil, 24° gravity oil would be a heavy spindle oil.

The tests for flash point and burning point were important in keeping every lubricant free of lighter and more volatile products.

Viscosity, or the measure of the body of the lubricant, was first taken by means of glass pipets im-

ported from England. Later, because of an accident where the chemist fell down while he was carrying practically all the standard viscosity glass pipets in this country, the Saybolt viscosimeter was invented, and this instrument is now the standard in all laboratories in this country.

These laboratory tests gave the oil a definite character, which formed the basis for improvements and served as the necessary units of measurements in refining. Later the chemists introduced methods for determining the chill or cold test, and for determining which oils would work the best with water, these latter tests being called emulsion tests. In connection with the emulsion test, it is interesting to note the error in the old saying that water and oil will not mix. Whenever water and some kinds of mineral oils work together in a circulating system, they not only mix, but sometimes will never separate.

All of these special characteristics had to be studied by the chemist, who had to devise ways of making the lubricants better so they would meet the more severe conditions being developed in commercial work.

The carbon residue test was devised by Dr. Conradson, a chemist. Motor oils forming the smallest amount of this residue in the engine were required; and it was necessary for the chemist to devise a measuring unit for the laboratory so the carbon residue could be studied and put under control.

With almost every advance in mechanics, and a consequent greater service demand on the lubricants, a method of measurement is devised by the oil chemist to enable him to work for the improvement of the oil.

As a result of this development we now have in the oil testing laboratory many different tests required for standardization work. Constant research is neces-

sary to keep products up to the practical demands of the machines in our varied industries.

Through this work the oil chemist is constantly improving the lubricants and the processes by which they are produced, the latest refinements being in distillation under high vacuum, where the crude is subjected to a comparatively low degree of heat for a short interval of time with a net result that oils free from burnt or decomposed particles are produced. Such oils do not have to be acid-treated as there is nothing objectionable to remove, as is the case where oils have been produced by the older destructive process of distillation.

The economies of the high vacuum system are considerable, greater production is possible, and since acid is not used the costly sludge and recovery problem is absent. Oils thus produced contain a maximum amount of the natural lubricant in the crude and are more fitted for the severe work they are called upon to do.

With these improved lubricants available, the condition exists that in many industries the lubricant has been more highly developed than the machine and the method of application. This slowness in the mechanical development is probably explainable by business economics.

Some limited classes of machinery have the highest types of lubricating systems whereby the best of the lubricants can be applied in the most scientific way. Other classes of machinery, even more extensively used, still have lubricants applied in the most primitive manner, and much can be accomplished in securing a better balance of these factors for the immediate future.

The general great classifications of industrial machinery are as follows:

Farming Machinery, used by 40 per cent of our entire population. Aside from general automotive machinery, this classification includes all general farm equipment which is constructed and lubricated in the primitive method.

Steam Railroads. The locomotives are lubricated by either grease or oil applied by hand-oiling methods. This places them in the first or primitive stage of lubrication development. On certain equipment siphon, wick, or drop oilers are used, and upon the axles of all passenger and freight cars where pad or waste is used to apply the lubricant, the development is in the third stage.

Electric Railroads, including power-house machinery. The modern steam engine, steam turbine, or Diesel engine equipment is in the fifth or sixth stage of development of lubrication; motor bearings and axles on cars using pad or packed waste lubrication belong to the third stage of development.

Marine and Stationary Power Machinery. Steam engines are in first or primitive stage for all hand oiling, with wick and drop oilers in the second stage. Diesel engines and turbine installation are supplied with forced feed lubrication and all apparatus necessary to bring lubrication to the last stage of development.

Industrial Production Machinery. The lubrication varies from the hand-oiling or primitive stage to the fourth or ring-oiling stage. In some classes of machinery the methods of application of the lubricant can never be greatly improved. In such industries as textile mills the present methods of oil application are most modern. In that particular industry friction is a great item, the amount of actual power required to handle the material being small and amounting to less than 15 per cent of the total. This has made it advisable to develop the lubricants and their application to the highest point.

Automotive. This is our most modern mechanical development, and the engines contain all of the most modern methods of applying the lubricants. Motor lubricants have been developed to the highest point. Results would be perfect if it were not for an element in lubrication known as contamination.

Contamination of Lubricant

When oils are placed on a bearing and allowed to run through and out, contamination is not a factor. When oils are stored in the lubricating system and used over again and again, contamination through various causes becomes a serious problem. Its solution has required the combined efforts of the lubrication engineers and research chemists. In contamina-

tion of lubricant in all industries the chemist determines the nature of the foreign material, which is then prevented from getting into the lubrication system.

With the first circulating systems attached to steam engines and later to steam turbines, the original cause of the failure of lubrication of these machines was due to water leaking into the oil system.

Engine builders could not conceive of such a condition, but the chemist showed that water, drained from the oil tanks in the base of the engines, had all of the characteristics of the water used in the steam boiler, and thus traced its source. Extra precautions were taken with later engines and turbines to prevent such leakages.

In the case of contamination of the oil in our automotive engines, there is a complicated condition that has required the attention of the full force of engineers and chemists in many allied industries in order to determine what is happening and to offer plans for correction.

Steam Turbines

When steam turbines were being developed there was continual difficulty with bearing lubrication due to contamination of lubricant. Gravity feed or pressure systems were used. The lubricants were put in small reservoirs in the base of the machine. The oils were not especially made to withstand emulsions or to separate from water, no such requirement having been developed for any previous form of machinery. It was found that the water from the condensed steam leaked into the oiling system, and as a consequence the oil and water were violently churned up at different

temperatures and pressures and completely mixed with air. It was also found that the water carried its proportionate part of the boiler deposits and that these organic and inorganic deposits would accumulate. All of this resulted in the oils emulsifying and sludge was left in the tanks and pipes. This was the cause of nearly all of the mechanical failures of the early turbines.

During the last fifteen years oils have been materially improved for turbine lubrication. The greatest improvement has been, however, in the methods of application which are designed to remove the water and foreign matter and to keep the oil clean and of the proper temperature. The almost perfectly lubricated bearings in a modern turbine installation in a battleship or super-power station are the result of much research work by the chemists and engineers of the oil industry, the engineers of the oil equipment companies, and engineers and chemists of the turbine and electric companies.

Turbine lubrication and turbine oils have been the subjects of investigation by government committees and of sections of the national engineering societies before which papers have been read by engineers and chemists who view this important matter from every angle. According to some of the latest published information from engineers operating our largest power stations there still seems to be room for improvement.

Automotive Engines

In the early days of the automobile, the fuel was very volatile, the end point of the gasoline being about 300°F. When any of this gasoline leaked by the

piston rings into the crank case of the engine it evaporated and did not combine with the lubricant to any noticeable extent. Sand and dirt taken into the engine through the carburetor did not cause comment or excessive damage because the body of the oil was sufficient to keep the surfaces apart and the dirt did not greatly interfere with the engine operation.

There has been a gradual change in the nature of the fuel, due to the tremendous annual increase in demand. The fuel now has an end point of about 440° F., and it is not all as volatile as formerly. Leakage of this fuel into the crank cases has brought about a decided complication in the lubrication of the motor. The heavier fuel leaks into the crank case in various amounts, combining with the lubricant and forming a thin mixture of oil and fuel. This contamination of the lubricant is referred to as dilution.

In the years to come the historian will write of the American men who built so many millions of automotive engines in a few short years that by 1925 the total yearly registration reached twenty million. These engines represent the greatest accumulation of research and industrial knowledge ever given a mechanical appliance, and yet every one of them is lubricated with a mixture of oil, fuel, water, and dirt that would not be used on the bearings of the most primitive farm machine.

The automotive dilution and dirt contamination problem is a serious reflection upon our engineering ability and, of course, it must be corrected.

This question of dilution and contamination is now attracting the attention of the engineering societies and is in course of correction. Other contamination problems just as complicated and as serious have been met and solved, especially with the steam turbine.

The Future

In nearly all important classes of machinery improvements in lubrication can and must be made, which will result in longer life of the machines, and less consumption of lubricants and power. This is an operation that is primarily within the province of the engineer. There has been a considerable lubrication development in the past which will act as a guide to what should be accomplished in the future.

With the present tremendous use of petroleum for fuel, and with a limited natural reserve, the day will come when we are faced with the necessity of securing a substitute for our present motor fuel. Chemists may well prepare themselves for that event which may not be far off.

As far as we have gone, no lubricants have been found for the most modern application systems equal to those prepared from petroleum. It may be that what petroleum is left in the ground, after the motor fuel substitute is found, will have to be reserved for the production of lubricants. At that time refining systems will necessarily be developed to produce economically the maximum amount of lubricant from those crudes.

Should the machinery of the future require more lubricants than the petroleum crudes will supply, then the development of nonfriction bearings and metals will have to be encouraged and the engineer and the chemist will be asked to work out suitable lubricants from shale deposits or from coal tars, or possibly combine the necessary ingredients for lubrication out of materials not now considered in that connection. Lubricants for the future should be made, so they will do more work than those we have today. The future

lubricants should last twice as long, and at the same time should reduce friction to a minimum.

For the present and the immediate future, conservation of lubricants and of petroleum fuels should be practiced so as to allow these valuable reserves to carry us as far as possible. This conservation program should include the production of automotive engines that will operate more miles to a gallon of fuel and lubricant. Apparatus should be developed and adopted to correct conditions that require the frequent draining of lubricant from these engines. The draining and present waste of the mixture of lubricant and fuel taken from twenty million engines is an economic blunder, equivalent to the careless burning down of our forest reserves, which is being reduced only through government supervision.

Conservation of machinery, of fuel, and of lubricant is now practiced in certain parts of our industry. These efforts need only be organized and extended.

Reading References

Day, David T., Editor-in-Chief. Handbook of the Petroleum Industry. John Wiley & Sons, New York, 1921.

Pogue, Joseph E. Economics of Petroleum. John Wiley & Sons, New York, 1921.

Southcombe, J. B. Chemistry of the Oil Industries. Constable & Co., London, 1913.

Thomsen, T. C. Practice of Lubrication. McGraw-Hill Book Co., New York, 1920.

The following files can be consulted at most public libraries:

Industrial and Engineering Chemistry, published by the American Chemical Society, Washington, D. C.

S. A. E. Journal, published by the Society of Automotive Engineers, New York.

Mechanical Engineering, published by the American Society of Mechanical Engineers, New York.

Journal of the American Society of Naval Engineers.

Journal of The Institution of Petroleum Technologists of London.

Lubrication, published by the Texas Company, 17 Battery Place, New York.

Publications of Vacuum Oil Co., New York.

Publications of U. S. Bureau of Standards and U. S. Bureau of Mines. (Secured through the Government Printing Office, Washington, D. C. Catalogs of these publications will be sent upon request.)

CHAPTER XIII

MATCHES

HUGO SCHAPIRO

Chief Chemist, The Ohio Match Company

It is useless to inquire in what way man first discovered that fire was subject to his control and could even be called into being by appropriate means. The discovery of the means of creating fire at will is, however, quite justifiably described as man's earliest achievement. Equally true is the statement that our present means of creating fire by the aid of a "match" is one of the greatest and most useful of human inventions. The development of the present-day match is a striking illustration of the application of scientific, especially chemical, knowledge to human needs.

HISTORY

A full appreciation of the usefulness and convenience of our present-day match is possible only after recalling the early methods of procuring and maintaining a fire or light. The difficulties were no doubt so great that in order to save trouble and labor the primitive man early hit on the idea of a fire which would burn day and night in public places. Carefully tended fires were kept constantly burning in the temples, and the sanctuary lamps of many modern churches are probably a survival of this custom, which originated in necessity.

One of the earlier and common methods of producing fire was by the friction of two pieces of wood. During a later period, however, fire was produced by friction of steel and flint, and for hundreds of years the tinder-box was the most convenient apparatus for producing fire. The use of splints dipped in sulfur, which were ignited by the sparks from the glowing rags, belongs to a later period. These splints are the forerunners of today's form of matches. They are, however, distinctly differentiated from present-day matches in that they had to be ignited from an outside source. In the beginning of the nineteenth century chemical reactions were first used to ignite a splint directly. The "oxymuriated matches" as they were called were comparatively successful and truthfully deserved to be called instantaneous lights, by way of contrast with the malodorous, aggravating, and inconvenient tinder-box. The invention of these oxymuriated matches was based on the discovery by Berthollet of the oxidation of combustible bodies by chlorates in the presence of strong acids. The instantaneous light box contained a bottle with some sulfuric acid, enough asbestos fiber to soak it up, and a supply of properly prepared matches. These matches were splints of wood which had been dipped into sulfur and afterwards into a paste consisting of chlorate of potash, powdered sugar, powdered gum arabic, and a little vermilion for coloring. By dipping these heads into the sulfuric acid, the matches were easily ignited. There were, however, many disadvantages. Sulfuric acid is destructive and therefore dangerous to use. It readily absorbs moisture and this soon reduces its usefulness. Frequently matches which had been dipped in the acid failed to ignite, and were returned to the box, where they came into contact with good

matches and ignited them all. Though these oxymuriated matches were an improvement over the tinder-box, they did not replace this method of producing fire.

The invention of friction matches by John Walker, a chemist of Stockton-on-Tees, Durham County, England, about 1826, practically drove all previous fire-producing methods out of use. The original composition of these matches is supposed to have consisted of chlorate of potash, antimony sulfide, and starch, the latter no doubt to act as a binder. A rather dangerous combination in the hands of the inexperienced! The great value of these first friction matches was due to the fact that they ignited upon being drawn over a piece of sandpaper. They were, however, not easily ignited, and since a great deal of pressure was required to produce the necessary friction, many heads were crushed or the ignition took place with explosive violence.

In the meantime efforts were being made to introduce phosphorus in a match composition. Phosphorus was discovered in 1669 by the alchemist Brant of Hamburg, who obtained it by distilling the residues from evaporated urine. Its preparation was long guarded as a secret and the substance commanded a great price until about 1770, when Scheele and Gahn demonstrated its occurrence in bone ash and prepared it from this source. The price of phosphorus soon became reasonably low, and since it was easily ignitable, this element was quite desirable as a source of fire. After many failures, successful friction matches containing white phosphorus were finally produced in the early thirties of the nineteenth century. The credit for this invention belongs to Dr. Charles Sauria of St. Lothar, who while a student at the College d'Arc,

Dote (Jura), made friction matches containing white phosphorus.

In the United States the first friction matches were made by Alonzo Phillips of Springfield, Mass., to whom the first U. S. patent for friction matches was granted in 1836. The heads of these matches consisted essentially of a little chlorate of potash, a great deal of phosphorus, a binder like gum arabic or glue, and some coloring matter. This composition easily ignited the sulfur-dipped sticks, the readily ignitable sulfur acting as a flame carrier from the heads to the wood. In a later period "parlor" matches became very popular. These matches contained less phosphorus and more chlorate of potash. The sulfur was in the meantime replaced by paraffin as a flame carrier. This substitution constitutes a distinct improvement. Paraffin volatilizes easily, its gaseous products of combustion are odorless, and its use does away with the irritating acid gases resulting from the combustion of sulfur. In 1905 the now familiar double-tip strike-anywhere matches largely supplanted the parlor matches. The tips of these matches contained, however, a large amount of white phosphorus.

While the introduction of white phosphorus was successful in solving the problem of producing fire at will, it brought a hazard to the match industry which, particularly in poorly ventilated work rooms, caused suffering among the workers, some of whom were unfortunate enough to fall victims of the phosphorus disease. This disease affected the jaw bones, resulting in necrosis. Attempts to regulate the match industry by legislation failed to eradicate the evil, and it was early recognized that the only safe way out of the difficulty was to substitute a nonpoisonous material for the dangerous white phosphorus. Numerous at-

tempts were made to find a substitute. These included the amorphous variety of phosphorus, called red phosphorus, which was discovered by v. Schrotter in 1845. The results, however, were not satisfactory, and white phosphorus was continued in use, without competition, until 1898, when a practical substitute was found in sesquisulfide of phosphorus. This compound was discovered in 1864 by G. Lemoine, and introduced in the match composition in France by Seven and Cahan. In the United States all strike-anywhere matches since 1913 have contained sesquisulfide of phosphorus in place of white phosphorus. Matches with white phosphorus are taxed in the United States so heavily as to make them practically prohibitive.

Types of Matches

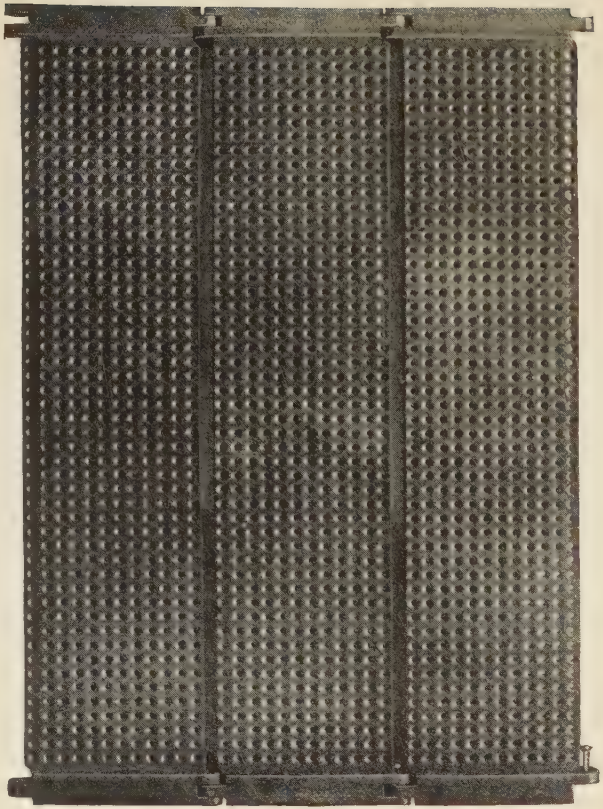
All matches are, of course, friction matches in so far as they are all ignited by rubbing them over a surface. There are, however, two distinct types of matches. One is the so-called "safety" match or "strike-on-the-box-only" match. In this class must be included book matches, where a thin strip of cardboard is substituted for the wooden splint. The other type is the "strike-anywhere" match. This is the most popular match in the United States. In the strike-anywhere match the easily inflammable material is compounded with the other match-head ingredients, and the reaction between the different components is started by the heat of friction developed by rubbing the head on nearly any surface. In the strike-on-the-box only or safety matches, the heads contain large quantities of chlorate of potash with some slow combustible, and ignition is caused by striking the match

on the sides of a box, the surface of which is coated with a composition containing red phosphorus.

Manufacture

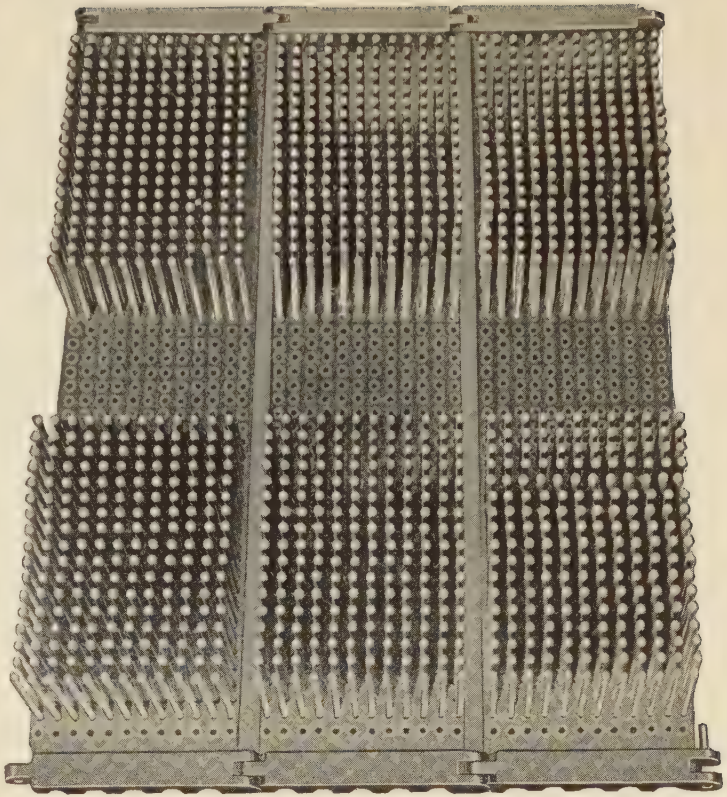
In the United States strike-anywhere matches are manufactured on a large scale to meet all its requirements. The continuous match machine cuts the sticks from blocks of wood. These blocks are fed into the machine in such a manner that the grain of the wood is nearly parallel with the up and down motion of the cutting head, which carries a series of dies and cuts the stick on its downward motion. The upward stroke forces the sticks, which are held in the thin die, into the holes of drilled metal plates. The plates are hinged together to form a long endless chain, in which the match sticks travel first to be "impregnated." This treatment usually consists of passing the sticks through a weak solution of ammonium phosphate and a subsequent drying in a hot-air chamber. The purpose of this treatment is to impart to a match stick the so-called "nonglowing" properties. A match stick thus treated will turn black immediately after the flame is extinguished. The endless chain next carries the match stick through a vat containing melted paraffin and then over a roller which carries the composition for the first head or bulb. A current of air helps to "set" the newly-formed heads. After traveling for some time, the now partially dried heads pass over a roller which in this instance carries the sensitive composition to form the ignition tip. This tip is smaller than the comparatively large bulb, which thus protects the tip from ignition by unavoidable friction.

The matches are then carried along for some time for further drying and back towards the cutting head.



Courtesy, The Ohio Match Co.

Empty Match Plate



Courtesy, The Ohio Match Co.

Full Match Plate

Shortly before the plates would again come over the cutting head, the matches are pushed out into a shaking trough, to be automatically delivered to the packing equipment. The filling into boxes, the placing of covers, and the wrapping are done by automatic machinery. The matches are never touched by human hands.

The Wood

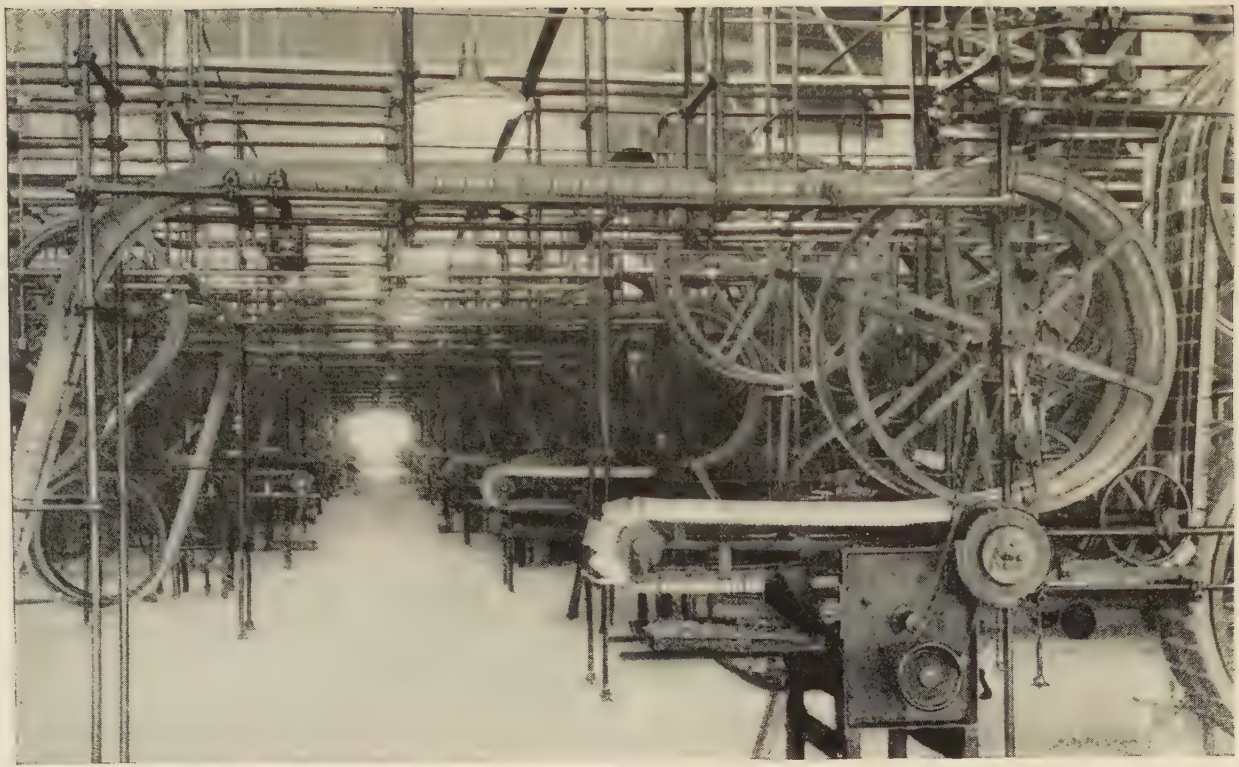
The wood is a species of soft pine, commonly known as white pine. This is a very large tree reaching a height of eighty to one hundred feet, and in some instances seven to eight feet in diameter. The main source of supply of match lumber is now the Northwest, where some of the large match manufacturers hold vast tracts of timberland in order to insure for their plants a supply of lumber for years to come. A prerequisite for the production of a good match is thoroughly seasoned wood. Seasoning not only decreases weight by the evaporation of water but increases the durability of the wood, prevents it from shrinking and checking, increases its strength and stiffness, and prevents it from staining. Seasoning is always in progress in open piles which permit a free air circulation over the lumber. Recently, artificial seasoning has been developed in the lumber industry and the match manufacturers are taking a keen interest in these developments with a view of adapting kiln seasoning to the needs of the match industry. The problems of seasoning of wood offer some interesting studies to the chemical engineer. The United States Department of Agriculture is carrying on some very important investigations in this field and has published some of the results in its bulletins.

The Match Head

The composition of the bulb is quite different from that of the tip. The large head or bulb is made of a slow-burning mixture which is difficult to ignite by friction. The tip, on the other hand, is made to ignite easily, and its rate of combustion and size of flame are so adjusted that the ignition of the bulb takes place without interruption.

Essentially, the bulb contains an oxidizing agent, chlorate of potash; oxidizable material such as sulfur and rosin; an oxidizable binding material such as glue; and filling material or diluents, as, for instance, ground glass. The tip on the other hand contains besides these ingredients a large quantity of sesquisulfide of phosphorus. When dry these mixtures are truly explosive. Since the purpose of all ingredients in the match head is to react only after the user strikes the match at will, the match-head composition must not undergo any spontaneous changes before or after forming the heads and drying. This fact brings many problems to the chemical department. To effect modification in the intensity of flame, rate of burning, sensitiveness to friction, rate of drying, resistance to moisture, etc., numerous other materials are used in addition to the previously named ingredients. Bichromate of potash, oxide of zinc, plaster of Paris, infusorial earth, starch in the form of paste, and clay, are some of the additional materials which by virtue of their chemical nature or physical state produce distinct effects on the resulting match composition. Aniline dyes are also used to give the match head a pleasing appearance.

One needs only to consider the complexity of a match composition to realize the variety of problems which present themselves to the chemist. The development



Courtesy, The Ohio Match Co.

Section of Match Machines

of the proper mixtures and the standardization of materials are essentially the work of the chemical department of a modern match factory. The influences which may and do change the physical and chemical character of the materials constitute a large field for study. The match composition must be of the right viscosity, it must permit the proper shaping of the heads, and must dry reasonably fast and uniformly throughout. The drying of the match heads is a problem in itself. The character and rate of drying of the match heads depends on the atmospheric conditions in the match room. The match machine room can be looked upon as a large atmospheric drier. Too high a temperature of the air in the room, particularly when the relative humidity is low, will cause a match head to dry rapidly on the surface with the formation of a flinty exterior. The results of such drying conditions are frequently disastrous for the product, as such matches will ignite with nearly explosive violence. This problem has been partly met by the chemist through modifications in the composition. During extremely bad weather conditions it becomes necessary to resort to air conditioning, with or without mechanical refrigeration.

The match head must have mechanical strength, it must not give off offensive gases, and it must also resist atmospheric influences reasonably well. All these requirements of a good match-head composition can be met only by scientific attack of the problems.

Chemicals

As a rule, the match manufacturers do not produce the chemicals which enter into the composition of the match head, but purchase them from various manufacturers. The larger match makers, however, do pro-

duce a few materials, which have an application almost exclusively in their own processes.

Glue is one important constituent, discussed elsewhere in this book. The amphoteric character of this substance, whose physical properties are changed by either acids or alkalies, makes possible many modifications of the physical properties of a match-head composition and brings the chemist into the field of research on the nature and behavior of colloids. A wealth of publications on this subject are available which now facilitate the study of this branch of physical chemistry.

Sesquisulfide of phosphorus (P_4S_3) is formed by slowly heating phosphorus and sulfur. The reaction is accompanied by evolution of heat. This compound, which as used in matches is free from white phosphorus, ignites in air at about 100° C. It is reasonably stable, and is practically unaffected by cold water. Boiling water decomposes it into hydrogen sulfide and phosphorous acid. The phosphorus used in the manufacture of sesquisulfide of phosphorus is a product of the electric furnace. Its source is phosphate rock (calcium phosphate) from which the phosphoric anhydride is liberated by silica and is immediately reduced to phosphorus by the carbon present in the charge in the form of coke.

Chlorate of potash is now produced exclusively by electrolytic processes. In the electrolytic cell for the production of chlorate of potash, which differs from the ordinary chlorine cell in that it has no diaphragm, the generated chlorine and potassium hydroxide react to form potassium chlorate: $3Cl_2+6KOH=KClO_3+5KCl+3H_2O$. This salt is easily freed from all impurities, and is used in the form of finely ground powder.

Future Developments

The American strike-anywhere match is no doubt the best match available for general use, and in its present form would appear to be hard to improve upon. A great deal of work, however, must be done to make this match more nearly ideal. The ideal match should burn with an absolutely smokeless flame, should generate no unpleasant odor whatsoever, and should resist moisture to such an extent that it will never be affected by atmospheric conditions. The materials entering into the match-head composition are of such a nature at present that efficient substitutes are highly desirable. Sesquisulfide of phosphorus is expensive. Glue should be replaced by a cheaper and if possible more efficient and less erratic binding material. The substitution of sodium chlorate for potassium chlorate is also desirable.

In this brief chapter on matches attention has been focused on the American safe strike-anywhere match because it is the type of match most important to the American match industry. The practically inert but larger bulb protects the smaller tip and makes this American match safer than the strike-on-the-box-only match, regardless of some belief to the contrary. The American match is at present the most convenient and safe match in existence. It is, however, not beyond improvement, and the field is open for further research.

CHAPTER XIV

PAINTS, VARNISHES, AND COLORS

HENRY A. GARDNER

Director, Scientific Section, Paint and Varnish Manufacturers' Associations of the United States, Institute of Paint and Varnish Research.

Prepared paints are made by grinding naturally mined or chemically produced pigments in oil, subsequently adding a thinner like turpentine or mineral spirits, and a drier made with cobalt, lead, or manganese to accelerate the drying tendency of the oil. Varnishes are produced by fusing fossil or recent resins, combining the "run" resin with heat-treated drying oils, and then thinning with a volatile product such as turpentine or mineral spirits. Driers, acting in a catalytic way to speed up the hardening of the varnish when applied, are also used in varnishes. This description briefly covers the methods of manufacture of the many ready-to-use products to be found in the average paint store. There are, however, over a thousand materials coming from all parts of the world, with which the chemist must be familiar in order to have a thorough knowledge upon which to base his processes and formulas. There is insufficient space in this book even to name these materials or the methods used, but a brief statement is given below regarding some of the more important products, their components, and their uses.

Twenty years ago there were only a few paint labora-

tories, and probably not over five or six paint and varnish chemists, while today there are probably over a hundred laboratories with from one to two hundred chemists who work almost exclusively on paint and varnish problems. This would indicate that chemistry is being recognized in the development of the industry.

History

We find in early literature suggestions regarding the use of protective coatings in the olden days. For instance, we have the entire pitching without and within of the ark by Noah preparatory to his sea journey, and we have evidence of the use as early as 2500 B. C. of paint compounds for the decoration of the tombs of the ancient Egyptians. The Greeks and Assyrians were also great believers in the decorative art, and later on the Romans developed great skill in the decoration of their dwellings. The very liberal use of color pigments in Pompeii and Herculaneum for the decoration of buildings and other structures is evident. The colors used in those days, however, were practically all earth colors such as red iron oxides, yellow ochers, siennas, lapis lazuli, and such products as might have been made from lead ores and naturally occurring mercury vermilion minerals or copper-bearing ores. Although there is no evidence that oil was not used in some of their colors, the majority were applied in the form of distempers, using the white of egg or similar albuminous substances for media. Records of the use of chemically produced pigments in early times have also been found, not only as cosmetics but for the decoration of surfaces. Senenius has stated that the ladies of Florence were prone to heighten their beauty

by the use of white lead, and he warned them against this practice.

White Opaque Pigments

Wilhelm Ostwald was probably one of the first chemists to apply scientific knowledge to painting problems, and in a series of letters addressed to a painter friend during 1903 and 1904, he explained many phenomena regarding the optical properties of pigments and liquid media that were at that time practically unknown. In one paper he explained why certain pigments are opaque when ground in oil. If the pigments cause the light rays to be refracted, and if the light-bending power of a pigment is similar to that of the oil, the light will pass through, leaving a transparent film. If the light-bending powers of the pigment are different from that of the oil—in other words, if the refractive index is greater—opacity is obtained. Oil has a refractive index of about 1.48, whereas opaque white pigments have a refractive index of about 1.90 to 2.2.

Of the white opaque pigments consumed in the paint-grinding trade, the best known are those made from lead and zinc. The so-called ancients knew how to make white lead, as will be shown by the following passage from Theophrastus (373-287 B. C.): "Lead is placed in earthen vessels over sharp vinegar, and after it has acquired some thickness of a sort of rust, which it commonly does in about ten days, they open the vessels and scrape it off, as it were, in a sort of foulness; they then place the lead over vinegar again, repeating over and over again the method. What has been scraped off they beat to a powder and boil for a long time, and what at last subsides to the bottom

of the vessel is 'Ceruse'." This old method undoubtedly produced a fairly satisfactory white lead, and it is interesting to note that the clay-pot method is still in use today but in a highly developed condition.

One can draw a vivid mental picture of Bartlett throwing a lump of galena into an open fireplace in Missouri and noting the evolved white fume condensing upon the brick, dreaming of a future industry based upon a subliming process. This product is now produced in large tonnage. It is probable that the average annual production of white lead pigments today is in the neighborhood of one hundred and thirty thousand to one hundred and fifty thousand tons, which indicates the very great growth of the industry.

In 1834, when Sorel was experimenting with galvanized metal, he discovered a fine white powder formed at the edge of zinc pots. Later records show the commercial production of this pigment by Leclaire in 1841 and its successful use in French house paints as far back as 1848. A direct method of zinc oxide production from ores at Franklin, N. J., was the basis of the tremendous industry that now flourishes in this country, and it is probably safe to state that the finest oxides in the world are now produced in America. It is believed that the annual production is well in the neighborhood of one hundred and fifty thousand tons. Zinc oxide has to some extent the same physical action in paints that metallic zinc has in alloys. When used with white lead, it overcomes the chalky tendency of the latter and keeps it much whiter in color.

Another valuable zinc pigment is known as lithopone, which consists of approximately 28 per cent zinc sulfide and 72 per cent barium sulfate. It is made by chemical precipitation and is of extreme whiteness and of very great opacity. It finds a very wide application

in the manufacture of interior flat wall paints, linoleum, oilcloth, shade cloth, and special paints of all kinds. Tremendous strides have been made by the American technologist in overcoming the light-sensitiveness of the grades produced years ago. This work marks an important era in the history of this useful pigment.

Other interesting white opaque pigments are antimony oxide and titanium oxide. The former is used only to a limited extent in this country, owing to the restricted amounts of antimony available for its manufacture. Titanium pigments, however, have come into quite wide usage. Their history is extremely interesting. Titanox is a white opaque pigment, recently discovered in America, which is produced from ores known as ilmenite and rutile. If you have ever picked up a handful of sand on a beach and allowed it to sift through your fingers or be blown from your palm by attending breezes, you may recall that the heavier particles remaining were sometimes of a black color. These were probably of a titanium base. Surface mining of the sands of Florida beaches yields much of the ore that is used in America, over a million tons probably being available for this purpose in one place. The pigment produced from this ore is remarkably fine in subdivision and is very white in color. Its hiding power is greater than practically any other widely used white pigment, having over three times the tinting power of white lead. It is unaffected by hydrogen sulfide gases and is therefore unexcelled for use in industrial communities when it is desired to maintain white, clean surfaces.

Metal Powders

Finely divided metal powders have a specific use as

Roof Exposure Tests, Including Daily Rain Spray.

paint pigments. Zinc powder (zinc dust), for instance, has been employed to some extent as a pigment, and for many years has formed a very substantial component of the anticorrosive paints used by the Navy Department for the bottoms of ships. In a similar way, aluminium powders have been used, being suspended in liquids which usually dry rapidly to form brilliant films. Both aluminium powder and zinc powder are excellent protectives of iron and steel surfaces, because they are strongly electropositive to iron, and when corrosion conditions are present, the zinc and aluminium powders tend to go into solution, thus protecting the iron.

Weathering of Paint

Careful studies have been made of the effect of various climates upon paints. Immense test structures have been erected for this purpose in many parts of the United States where the prevailing weather conditions were of a markedly different nature. These tests demonstrated the fact that the summer months cause much more rapid wearing of paints than the winter months, and that the side of a dwelling facing the sun and the strong prevailing winds is more rapidly affected than the other sides. The tests have also shown that more durable results are almost universally shown with tinted paints than with white paints. Permanent coloring materials ground in a white paint base have the effect of preventing chalking and thus increasing the longevity of the paint.

An inquiry made a few years ago in the Middle West as to the value of paint upon farm buildings developed information that bankers would lend from 5 to 50 per cent more upon land where farm buildings were well

painted and kept in good condition than where they were not. It was maintained that the painted buildings were an indication of thrift, and that a thrifty farmer was a good client to whom money could be safely loaned.

Research on Metal Protectives

Extended researches have indicated that corrosion of metal is due very largely to electrolytic reactions, and that the protection of metal with paint depends upon the use of pigments which are rust inhibitive in character. These are usually of the basic type which inhibit corrosion, or of the chromate type which tend to make iron and steel passive to electrolysis. Pigments of the carbonaceous type, when placed directly upon metal surfaces in the presence of moisture, may tend to excite or stimulate corrosion rather than retard it, although such coatings are invaluable for use as subsequent coaters over properly designed primers of the inhibitive type.

Varnish

The derivation of the word "varnish" has been ascribed to Berenice, the beautiful blond wife of an early king of Egypt. It has been stated that she sacrificed her beautiful hair in the Temple of Venus in fulfilment of a vow for her husband's safe return from a campaign. The hair disappeared from the altar, and was discovered by an astronomer as a constellation in the Milky Way. Amber was likened by the Greeks to Berenice's hair. Note the Latin word "vernix" and its later Italian form of "vernice." When we think of varnish, there comes to mind a pale amber-colored

fluid that dries, when applied, to a thin, tough film of high luster. To one who has studied chemistry or art, there may come a further mental impression of chips of amber from ancient pipe stems being melted in oil in a chemist's shop to provide a few ounces of varnish for the pictures of Rembrandt or some other old master or for the finishing of the violins of Stradivarius. Amber, however, is no longer used in commercial varnishes.

Esterification

Resins that are used in the manufacture of varnish, such as rosin and the harder fossil resins (Congo, Manilla, Pontianac, Kauri, etc.), are all highly acid, usually having an acid value of 100 to 150. Naturally they produce varnishes which are rich in organic acids and which may tend to "liver" when ground with white pigments of a basic nature. Marked livering unfits a paint for use, the product becoming almost solid. In order to prevent this effect and produce resins that are even more waterproof and resistant to alkali, the chemist has resorted to the production of so-called ester gums which are made by combining the highly acid resins with a substance such as glycerol which will form a neutral product. These esters are now in very wide use. Thus by a comparatively simple process, the chemist has transformed these highly acid substances into more useful products.

Rubber Latex

Among the interesting materials that have during the last few years been proposed for use in the paint industry is rubber latex, or the milk as it comes from the rubber tree. This material, in a slightly alkaline

condition, is shipped into this country in large quantities for use in the rubber industry, and experiments would indicate that it may ultimately find a possible field of usefulness in the paint industry. Through the introduction of certain pigments, products can be made with this material which have a very promising future, drying very satisfactorily to films having marked waterproofing effects. The latex usually contains about 28 per cent of rubber, 2 per cent of resin, and very small amounts of protein and sugar, the balance being water.

Furfural

Another interesting product that has recently come into use by the industry is furfural, a liquid produced from waste corncobs by cooking under pressure with steam, or from other waste food substances. It has been found that furfural has a very marked solvent action on dried paint and varnish, and can therefore be used to remove paint films from old surfaces where refinishing is desired. It has also been found that furfural is a very remarkable solvent for nitrocellulose, and will take into solution a very great quantity of this interesting material to form a liquid that may be applied as a constituent of automobile lacquers. The very slow drying rate of furfural, however, limits its use.

Marine Borers and Barnacles

When small boats made of wood are placed in salt water in many localities, the timbers are almost entirely honeycombed by marine borers such as Teredo or Limnoria, in a very short period of time, if left in the uncoated condition. It has been found through a very extended series of tests that this condition can be

Tests on Submerged Plates with Protective Coatings.

entirely prevented through the occasional application of quick-drying spirit paints containing 10 or 15 per cent of copper or mercury oxides as a constituent of the pigment portion. The prevention of the destruction of cellulose fiber by these molluscan or crustacean borers rests to some extent upon the destruction of the embryo. A film that continuously gives forth the proper concentration of toxic salts is the one that gives the best results. Similarly, special paints have been developed for protecting the steel bottoms of naval vessels as well as those of the merchant marine. These foul up very rapidly with barnacles of which Darwin and Pilsbry have defined several hundred species. Bryozoa, ascidians, and similar growths also tend to aid the barnacles in forming on the bottoms of these ships dense masses which greatly retard their speed and increase fuel consumption. It has been found, as a result of recently conducted tests on several thousand panels with compositions containing every known toxic under the sun, that satisfactory results can be secured with properly designed coatings. Those spirit paints that become slowly soluble in the water or slough off gradually, carrying the toxic constituents such as cuprous and mercuric oxides into the water, have given the most efficient results. Curiously, some of the tests have indicated that paints of a highly light-reflective type, such as white and light tints, are more efficient than those of dark color, which would indicate certain color preferences of the barnacles in their embryonic state. More curious, however, is the fact that barnacles seem to disregard the Volsteadian three-mile limit and are seldom to be found at distances greater than three miles from shore. This is due to the fact that they must become attached in their embryonic stage to some floating or rigid substance or they cannot live.

Lacquers

Tremendous strides have been made by chemists during the last few years in the production of quick-drying coatings. These were originally used in the form of dopes consisting of about six ounces of nitrocellulose in a gallon of solvent, and were as a rule rather viscous. In the last few years there has been developed a newer type of nitrocellulose known as the low plasticity type, which is of such a nature that as high as forty ounces may be obtained in solution in a gallon of solvent, with such mobility as to allow of application. It is produced by regulating the nitration or by reducing the viscosity of the product in solution under pressure. Whereas the old-style dopes gave thin films which were of but short durability, the new type, because of the great amount of solids present, is of good durability and has therefore come into wide use in the automobile industry. Its use greatly speeds up production in many plants where the cheaper types of automobiles are produced and where great brilliancy and gloss are not a controlling factor. The solvents used in these lacquers bring to the paint and varnish chemist materials of which he has heretofore had but little knowledge. Some of these solvents are amyl acetate, butyl acetate, ethyl acetate, anhydrous alcohol, butyl propionate, ethyl lactate, diethyl carbonate, and such film plasticizers as tricresyl phosphate, triphenyl phosphate, diethyl phthalate, butyl phthalate, and butyl tartrate. Concentrated solutions of nitrocellulose in such solvents and plasticizers are mixed with various solutions of resins and then pigmented to form colored coatings which dry with extreme rapidity. The paint chemist has thus added to the almost unlimited list of materials he produces a new product which is made from

a raw material (cotton) produced to a greater extent in America than in any other country in the world. Almost unlimited supplies of vegetable matter, from which various solvents can be produced by synthesis or by bacterial action, guarantee that the production of such lacquer products in the future in America will be well taken care of.

Cause of Color

Color as one perceives it when he looks at a painted surface or a painted object is simply a psychological or optical sensation. You say, for instance, that lampblack is black. The sensation is due to the fact that the structure of the pigment has caused the absorption of nearly all the visible light rays that fall upon it. When these same light rays fall upon white zinc or white lead, they are practically all reflected, and we say that this pigment is white. Similarly, we have a sensation of red from a pigment which absorbs all rays except those that give the sensation of red, while from a green pigment we have reflected only those rays that give the sensation of the particular hue of green that appears.

Stieglitz has recently pointed out that color is due to the absorption of the visible light waves by electrons vibrating within the confines of a reducing atom, and held loosely enough, as a result of the proximity of the oxidizing atom, for the vibrations necessary to the absorption of such long light waves. Upon this fundamental conception may be based many developments toward the production of colors in the future. How simple would be the preparation of all chemical colors for use in the paint industry if we could by a simple process change the physical structure of carbon so that it would reflect red, green, or blue in such propor-

tion as to give the hue we desire. This is a problem for the chemist-physicist that offers great rewards.

Several hundred colors of various kinds are produced in the chemical industry for use in paints and varnishes and similar purposes. The principal ones, however, are the lead chromates, Prussian blues, chrome greens, and the various lakes made by precipitating such dye bases as paranitraniline or toluidine upon barium sulfate or similar earth pigments.

Many people do not have a very well defined idea of color, and, as an indication of the necessity of some method of defining color more closely, there is given below an abstract from a letter written by Robert Louis Stevenson while at Samoa:

> Perhaps in some way it might amuse you to send us any pattern of wall paper that might strike you as cheap, pretty and suitable for a room in a hot and extremely bright climate. It should be borne in mind that our climate can be extremely dark, too. The colour in favour of its proprietor at present is a topazy yellow. But then, with what colour to relieve it? For a little work-room of my own at the back I should rather like to see some patterns of unglossy—well, I'll be hanged if I can describe this red—it's not Turkish and it's not Roman, and it's not Indian, but it seems to partake of the two last and yet it can't be either of them because it ought to be able to go with vermilion.

Effect of Color

It has been found that a very great difference exists in the temperature which may be maintained in gasoline and similar light-oil storage tanks through the adoption of light colors for the outside. Years ago nothing but black paints or dark reds were used for this purpose. The evaporation loss of naphtha in summer weather was very high. Through the adoption of light colors, the temperature of the naphtha could be kept at least ten or twelve degrees lower and the losses cut down something like 60 per cent. In many of the

oil-producing regions where refineries are located large quantities of hydrogen sulfide gas may be present, and for such regions white paints free from lead are used. In some cases paints of the aluminium type are also applied.

The difficulty that is often experienced in obtaining sufficient coal for heating purposes suggests to the consumer the importance of using every safeguard to conserve fuel values. That the color of the radiator may have some direct effect upon the situation, at least from the standpoint of increasing the efficiency of transmission of a radiator in the home, is apparent from recent tests which show that color has a very pronounced influence in this regard. These tests indicate that bare iron radiators or those coated with dark-colored paints or aluminium or bronze paints give the least radiation, while white or light-tinted paints give the highest amount of radiation. It is probable that a very great tonnage of coal throughout the United States could be annually saved through the adoption of this modern principle of coating radiators with white or light-tinted paints, and that homes could be kept very much warmer during the winter period.

Colors and Light Reflection

In addition to the antiseptic value of interior painting, the subject should be considered from the standpoint of illumination and psychological effects.

Decorators usually choose for rooms in which people spend most of their time colors likely to induce the most cheerful frame of mind or to give the most restful effects. That the influence of light colors may also have a pronounced effect upon the increase or decrease of body weight of an individual, would appear

possible from some tests that have been made during the last few years, which seem to show a relationship between the weight of people and the color of the rooms they occupy. Increase of weight is generally caused where colors of high luminosity—whites and light tints—are used, whereas decrease of weight is indicated where colors of low luminosity—blacks and dark shades—are used.

The color of interior walls of a room constitutes a more important factor than the type of illuminant used. This is shown by the fact that the illumination of an interior space lighted by a tungsten lamp can be made to vary from something like 12 to 88 per cent total reflection by applying different wall colors ranging from white to very dark green. The illumination of factories, railroad terminals, stores, office buildings, and all similar places can be greatly increased by the application of such colors. In schoolrooms and hospitals very careful selection should be made, otherwise physical fatigue will result. Dark colors such as brilliant reds, browns, and dull grays may be the active cause of lessened efficiency, nervousness, etc., whereas very light tints of cream, blue, and green greatly stimulate activity and are conducive of happiness and amiability.

Sanitation

From the standpoint of sanitation and hygiene, painted walls are to be recommended. Usually both tenant and landlord are oblivious to conditions that cannot be readily seen and detected. From many tests that have been made, the writer is convinced that one of the most efficient means of destroying bacteria in quarters previously occupied by persons suffering from contagious disease is to be had by painting the

rooms with an oil-pigment paint. The vapors from such paint develop formaldehyde, an antiseptic which is fatal to bacilli. In hospitals where it is necessary to maintain sanitary conditions, the walls are invariably painted with paints that can be frequently washed.

It is rather interesting to note that paint may serve as a direct aid to proper acoustic conditions. When sound waves impinge upon a surface coated with several coats of paint, much of the sound may be absorbed. Several coats of paint in which cork is embedded have been used with very marked effect in this connection.

Producing Our Own Materials

Aside from linseed oil, the oils that are used most widely in the paint and varnish industry come from foreign countries. Attempts have therefore been made during the last few years by the paint and varnish industry to grow in this country oils that have been imported in large quantities from the Orient. The most important of these is tung oil or Chinese wood oil, a product crushed from the fruit of a tree that grows wild on the hillsides of southern China. When the nuts are crudely expressed by the Chinese, there is obtained a very viscous, amber-colored oil. Probably 80 per cent of the production of China comes into this country, amounting to over twelve million gallons a year. It is used in America as the base of practically all modern waterproof, quick-drying varnishes. Its successful introduction apparently dates from the time when the fossil gums imported from New Zealand and other points were growing scarce and expensive. It was found that through the use of tung oil, varnishes could be produced in connection with

American rosin, that for some purposes were even more satisfactory than the high-grade varnishes heretofore produced from expensive fossil resins and linseed oil. A few years ago some tung oil seed was imported and planted in various southern localities. A visit to these places indicated to the writer that the most prolific growth was shown by seed planted in northern Florida, full-sized trees being grown in a period of about eight years; many of them coming into substantial bearing in about three or four years. With this as a start, the American paint and varnish industry has during the past two years set out from seed produced in Florida, over one hundred thousand trees at a point about eighty miles southwest of Jacksonville. It is very fortunate that this start was made in the production of American tung oil, as it is apparent that foreign disturbances at any time might restrict or harass shipments from the Orient. During the last few years prices of this oil have at times been raised to an almost prohibitive point.

Such an effort to foster local production on scientific lines might well be compared to the growing of plantation rubber. It may be remembered that a few years ago Brazil exported about twenty-one thousand tons of rubber, which was practically the world's production. From a few seeds brought to England by British subjects, seedlings were obtained that furnished the basis for the immense plantations in Borneo, Sumatra, and Malay. Today there are produced annually over three hundred thousand tons of rubber, 90 per cent of which comes from those British possessions to which the seedlings were transplanted. This start in the production of American tung oil for the paint and varnish industry promises well, and under proper cultural conditions it is probable that there will be pro-

Tung Oil Trees Eight Months Old from Planting Seedlings. View of One of the Groves in Northern Florida.

duced in this country very much better and stronger trees, with better yields, than are grown in China. Crushing tests already show that the oil produced from the domestic nuts is far superior to that imported from China. This is largely due to the modern methods of crushing available here.

The flax that furnishes the linseed oil to the paint and varnish maker is grown in the northwest section of the United States, and, although a large quantity is produced in this country, we are still compelled to draw our supply very largely from other countries such as South America, where the bulk of the world's crop is produced. With the gradual falling off from year to year in the production of flax in the United States, only about nine million bushels were produced a few years ago. As a result, however, of efforts of representatives of the industry working with state agricultural colleges in the West, a study was made to determine the causes of low yield per acre and the effect of various diseases. As a result, during the past year the crop has been brought back to approximately the normal yield of about twenty-five million bushels.

Soy bean oil is another oil used to some extent in the paint and varnish industry. It is imported from Manchuria. During lean years in flax production, research work indicated that this oil could be utilized in the paint and varnish industry. Through work with agricultural colleges, the paint and varnish industry assisted in the growing of soy beans for their oil content, and as a result there are being produced in the United States about eight million bushels of domestic beans. Production is increasing annually, and it is believed that sufficient beans could be grown in America to take care of the entire demand of the paint and varnish industry. Similarly, experiments on growing the plant

that produces perilla oil are being conducted in this country. This oil is superior even to linseed oil as a drying oil for paints. It is used very widely in Japan for oiling paper. Experiments are also being conducted almost continuously with other oil seeds, with new and interesting resins, waxes, pigments, and other materials brought to the laboratories of the industry from all parts of the world.

War-time Importance of Paint and Varnish

When the accomplishments of industry in the Great War are recorded, a statement may appear to the effect that the conflict was prolonged by paint and varnish, and that these materials had a direct bearing upon its ultimate outcome. Such a statement will seem less startling to a person who will look back over the exciting incidents that filled the four years of strife, to the closing days of 1914, when the Germans were finally checked at the Marne. Another week would perhaps have marked the end of the war, had it not been for the ability of the Allies at this time to provide more men, ammunition, and equipment. It was at this point that paint played its role, since practically every implement used in modern warfare might have a useful life of something less than a week, unless protected by paint and varnish. The rains and fogs of September might overnight have rendered useless much of the equipment of the opposing forces had it not been for the preserving properties of paint.

The stability of aircraft depends upon the maintenance of wing and control surfaces that are light and of rigid form. It is certain that the airplane could not have been used in warfare, had it not been for the protective properties of paint and varnish, applied to the

linen or cotton cloth that was used for covering the immense wing surfaces. It is impossible to make this cloth sufficiently taut by stretching. Moreover, it is subject to rapid absorption of moisture and may become flabby upon short exposure. To overcome this condition, there are applied to the cloth-covered surfaces four or five coats of airplane dope, consisting of cellulose acetate or cellulose nitrate (the latter being a form of guncotton) dissolved in rapidly evaporating solvents such as acetone, methyl acetate, and similar esters. These dopes are made plastic with such materials as triphenyl phosphate. When they are applied, they rapidly dry, producing films that shrink the cloth to a drum-taut condition on the wings. Even when this is accomplished, it is necessary to paint or varnish the treated cloth to protect it further from water and keep it in a permanently rigid form. The pigments used in the paint shut out the actinic rays of light which otherwise would penetrate a transparent film and rapidly disintegrate the coating and cause quick decay of the cloth.

It may also be pointed out that the spruce strength members of airplanes, the spars and beams, might warp out of shape and throw the surfaces out of alignment after a few days' exposure to moist conditions, if left bare. Moreover, practically the entire body or fuselage of an airplane is constructed of extremely thin ply wood (veneer) consisting usually of three laminations of one-eighth-inch stock, glued together. Without paint or varnish protection, the life of such parts would be brief, especially when exposed to conditions such as obtain along the seacoast. The more modern planes, constructed of light alloys of aluminium with small amounts of copper and manganese, also show very rapid disintegration when left in an uncoated

condition. It has been found, however, that the life of these may be prolonged for a satisfactory period through occasional applications of varnishes. The metal fittings, the stay wires, and the control cables used on aircraft also require protection with paint and varnish in order to prevent rapid corrosion and subsequent diminution of strength, the lowering of which would add greatly to the risk of flying. As high as three hundred gallons of dope, varnish, and enamel are sometimes used upon some of the larger sized planes.

The modern dirigibles, such as the "Los Angeles" and the "Shenandoah," are made of duralumin framework which must be kept well coated with paint and varnish to avoid rapid decay. Inside of this framework there is a large number of gas bags to hold the hydrogen or helium gas. These bags are constructed of light-weight cotton upon which goldbeater's skin is placed through the use of either rubber or gelatin adhesives. As an additional requirement, the gas bags are properly coated with a very flexible waterproof varnish to increase the gas resistance and diminish the possibility of moisture effects. The outer surfaces of these dirigibles are made of light-weight cotton which must be doped into place in order that sufficient tautness may be obtained to prevent "bellying" by winds. There is then applied a protective coating containing aluminium powder, which shuts out the active rays of the sun and thus keeps down the temperature of the gas. This coating also greatly prolongs the life of the fabric.

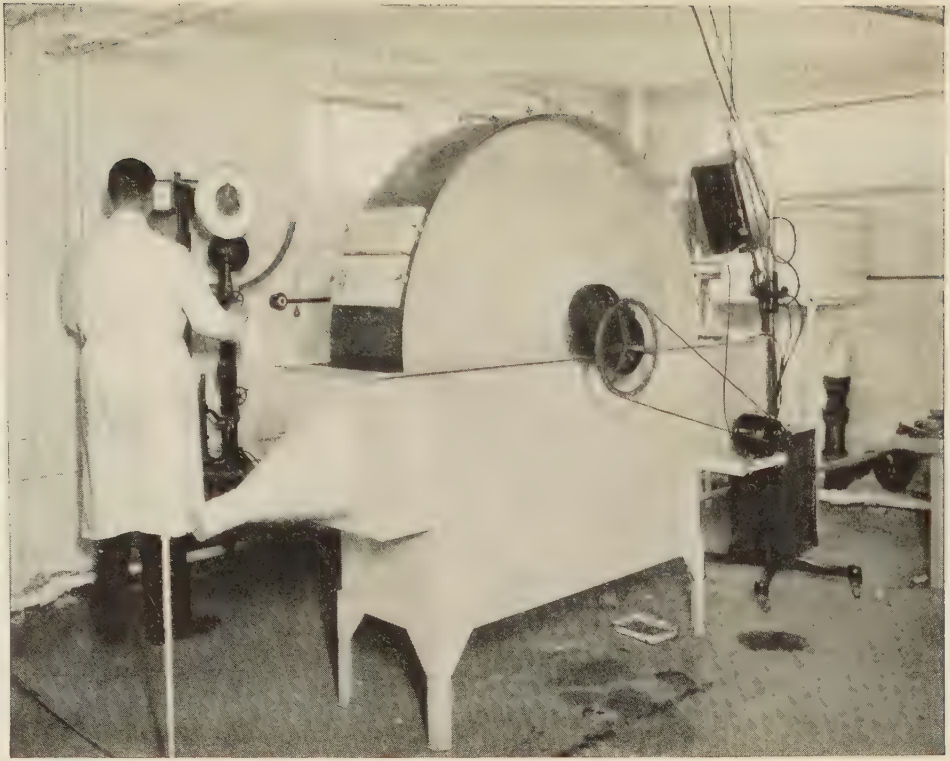
Modern high explosive shells are filled with picric acid or trinitrotoluene mixtures which have the property of acting upon the iron surface of the shell to form compounds that are extremely unstable and subject to premature explosion. In order to prevent the forma-

tion of such products, the interior of all shells must be coated with a varnish that will act as an insulating film. These are usually spirit varnishes made with shellac, collodion, or bitumen in light solvents, and sometimes compounded with linseed or tung oils. They are baked or stoved to give hard, tough films. The exterior surfaces of all shells are painted. If left bare and stacked in the field for long periods of time, they would show rapid corrosion which might possibly interfere with their loading into the guns. Another important reason for painting is to afford means of identification of each type of shell, and for this purpose a series of colors is used, which are bright and readily recognizable. These colors differentiate the high explosive, shrapnel, illuminating, gas, anti-aircraft, and other types of shells. Requirements for extreme rapidity in drying must be observed. The paints applied usually dry hard in not more than one hour.

There were produced in this country during war time over twenty million cartridges per day, and every one of these required varnish protection. The interior of the neck of the cartridge usually must be coated with varnish in order that a tight seal may be formed where the cupro-nickel bullet is fixed and thus prevent the admission of moisture to the powder in the shell. The primer cap on the end of each cartridge is also sealed with the same varnish in order to maintain the sensitive primer mixture in a dry and functionable condition. It is rather interesting to note that when unvarnished cartridges reach the temperature of a hot summer's day, the air contained within the shell expands, and if the cartridge is then cooled off by placing it in water, a vacuum is immediately formed; water is then sucked in at the neck or around the primer, and the powder may be rendered inactive. With the mod-

ern varnished bullet, however, it would probably be safe for the soldier campaigning in the Sahara Desert to place his cartridges in a tank of water overnight without fear of rendering them defective.

Ships of war are ships of steel, but this metal is only serviceable as long as it is protected from corrosion. Paint protection is therefore a necessity to the successful operation of a battle fleet. To the uninitiated it might seem rather surprising to learn that the coating of one large ship may require over one hundred tons of paint, and that the paint in many parts of the ship is renewed practically every three months in order to maintain permanent protection and a bright, up-to-the-minute appearance. The steel, wood, and concrete vessels of the merchant marine, the army transports, the submarine chasers, and every other type of craft used in warfare require some type of protection. While much of the paint applied during war time was for the purpose of camouflage, which was found successful in rendering craft optically elusive to the prowling submarine, the main object was protection against the elements. At no previous time in the world's history has color played so important a role as during the war period. This art was developed practically overnight and became one of the most important considerations, receiving the attention and application of some of the world's most talented marine artists. The lives of thousands of wounded troops confined in hospitals were often saved through the skill of the camoufleur in concealing, by clever coloration, the roofs of buildings from the view of hostile aviators. The successful voyages of vessels and troop ships with their much-needed cargoes may also be attributed in large measure to the modern developments in surface-craft coloration. The hiding or making elusive by optical distortion of guns,



Apparatus for Accelerated Tests on Paints, Varnishes, and Colors. Cycle Includes Water Spray, Cold, Heat, and Ultra-violet Light.

aircraft, and nearly every conceivable type of instrument of warfare depended to a great extent upon the use of camouflage paint. Highly important discoveries were made in the optics of paint pigments and many applications of scientific principles were called upon in working out special formulas, the history and importance of which it is probably yet too early to disclose. The auto truck, tractor, and general mobile equipment used for the transportation of ammunition and men would have been inefficient unless protected with paint, and one may imagine how long the spokes of an artillery wheel would have retained their form when subjected to field usage, if left in an unvarnished or unpainted condition. It is not difficult to visualize the amount of warping and rotting of wood parts or the corrosion of bare metal parts that would take place.

Testing Methods

Some of the tests that are now run upon pigments, oils, and other liquids used in the paint industry are as follows: tensile strength and elongation of film; hiding power; brightness; film thickness; specific gravity; fineness; bulking value; oil absorption; texture; viscosity; surface tension; and microscopic condition. The analysis of finished products is followed by a determination of durability by roof exposure tests and by accelerated exposure tests such as are indicated in the accompanying illustration.

Through the efforts of the paint and varnish chemists of America, important technical work is now arranged through several organizations. Included among these is a very active committee on protective coatings of the American Society for Testing Materials, which has to do with the development of knowledge regarding the

materials used in the industry, the standardization of specifications, and methods of testing. Work carried on by this organization over the last fifteen years has resulted in much valuable information. There is also a recently formed paint and varnish division of the American Chemical Society and at recent meetings there has been an average attendance of a hundred and fifty chemists from the industry. At these meetings, papers of general interest relating to scientific achievements from the various laboratories are presented. There also functions an organization of paint and varnish production men in twelve different paint centers of the United States, at which monthly meetings are held to discuss problems of a general nature, relating to raw materials, plant processes, and methods of testing.

Chemico-Mechanical Aids

Through the efforts of chemists with a mechanical turn of mind, many recent developments have been made in the paint and varnish industry in the adoption of modern types of machinery. In the varnish industry, for instance, instead of depending on the old-style filter press for the clarification of varnishes and oils, there are now used high speed centrifugals of various types which have become most efficient in removing suspended matter and producing products of a high degree of clarity. Similarly, most fine enamels are subjected to filtration in order to remove agglomerates of pigments as well as foreign matter which would give a rough appearance to the film.

The pebble mill for grinding large quantities of paints and enamels with low labor charge has come into rapid use. While the old-style burr stone mill or plate mill has not been entirely replaced by the pebble

mill, the latter has come into very wide use and is occupying a very prominent place in the industry. The colloid mill is now being experimented with, and it is probable that this mill may be adopted for many products.

Fume Recovery

Industrial economies often result from the influence of external conditions. For instance, the aromatic pungency of atmosphere that evidences the presence of an oil or gum-using industry has been responsible for attempts, more or less successful, to "bottle the smell." The resulting elimination of objectionable fumes or odors has often been accompanied by recovery of useful products. These fumes may be of the uneconomic types that are condensable through the installation of apparatus and processes but which do not yield products of sufficient value to pay the charges on the installation or cost of operation. On the other hand, industrial fumes may be of the economic type and may occasionally yield by-products of considerable value. It is well known that there is a very serious fume loss in the boiling of oils in the making of varnish. In the running of the resins it is very often found that as much as 20 to 25 per cent by weight of the resin must be lost in fume before it becomes soluble in linseed oil. With the object in view of recovering these products, as well as rendering varnish plants less "smelly," extensive apparatus has been designed in this country, and economically installed at many varnish plants. Recovery of the volatile matter during thinning operations on hot batches of varnish has also afforded dividends to the varnish maker in the form of many thousands of gallons of turpentine and other similar products that have been initially lost as fume.

Metals for Varnish Kettles

Although copper and steel are used to the greatest extent in the construction of varnish kettles, aluminium has of late years found great application. Its low weight as well as its nondarkening effect upon varnishes is well known. It is, however, less resistant to the action of heat. Recently kettles made of nickel and monel metal have come into wide use in the varnish industry, and monel metal has proved exceptionally valuable because of its strong resistance to the burning-out action of heat. Its heat conductivity and the fact that it is unacted upon by the highly acid organic acids in resins, which would discolor iron or copper kettles, make monel metal desirable for this purpose.

Spraying Paint

The war placed great demands upon the paint industry, and it was found necessary to use every means to accomplish the huge painting program that developed. The shortage of men capable of wielding brushes soon became apparent, and greater speed was demanded in production. As a result, the steel hulls of many vessels, the rough siding of many temporary buildings, and the surfaces of thousands of guns, tractors, and other military equipment were coated by the spray machine. In this operation, paint is forced by air pressure from a small tank to a gun, and there distributed in the form of a very finely divided spray, enabling the operator to coat surfaces in probably one-fifth the time that the paint could be applied by hand brush. The principle is similar to the application of perfume from an atomizer. Today this method of painting has come into very wide use throughout the

country, and the interiors of practically all factories where there are available large surfaces, are now coated by the spray-painting machine. Journeymen painters at first objected to the use of any appliance which they thought might cut down their occupation. It is believed, however, that such a device will really greatly stimulate the employment of and demand for painting labor. Comparison of the situation might be drawn with the effect of the sewing machine upon the tailoring industry. The journeyman tailor at first looked askance upon the development of this machine. It was soon found, however, that the machine created an almost entirely new industry in the production of ready-made clothing, and the availability of this product at once resulted in a tremendous demand and an increased output. As a result, thousands of operators were required where hundreds were employed before. Similarly, it is believed that any device which creates new business in its field of operation is to be given hearty support.

Reading References

Cushman, Allerton S., and Gardner, Henry A. Corrosion and Preservation of Iron and Steel. McGraw-Hill Book Co., New York, 1910.

Gardner, Henry A. Paint Technology and Tests. McGraw-Hill Book Co., New York, 1911.

Gardner, Henry A. Paint Researches and Their Practical Application. P. H. Butler, 2201 New York Ave., Washington, D. C., 1917.

Gardner, Henry A. Papers on Paint and Varnish. P. H. Butler, Washington, D. C., 1920.

Gardner, Henry A. Physical and Chemical Examination of Paints, Varnishes and Colors. P. H. Butler, Washington, D. C., 1925.

Hurst. Painters' Colours, Oils and Varnishes. J. B. Lippincott Co., Philadelphia.

Lewkowitsch. Chemical Technology and Analysis of Oils, Fats and Waxes. The Macmillan Co., New York.

Livache and McIntosh. Manufacture of Varnishes. Scott, Greenwood & Sons, London.

Morrell. Varnishes and Their Components. Henry Frowde and Hodder & Stoughton, London.

Seeligmann and Zieke. Handbuch der Lack- und Firnishindustrie. Union Deutsche Verlagsgesellschaft, Berlin.

Zerr and Rubencamp. A Treatise on Color Manufacture.

Bulletins Nos. 1 to 51 of the Scientific Section, Paint Manufacturers' Association of the United States.

Circulars Nos. 1 to 240 of the Scientific Section, Paint and Varnish Manufacturers' Associations of the United States.

Reports of Committee D-1, American Society for Testing Materials, 1903 to 1925.

CHAPTER XV

PORTLAND CEMENT—A CHEMICAL CONTRIBUTION TO MODERN CONSTRUCTION

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Anyone who has watched the construction of a modern building has observed a group of working men mixing together sand, gravel, a gray powder poured from bags, and water, until the whole mass of material has the consistency of gruel. Following this operation the gruel has been carried away in barrows and dumped into a hollow wooden form, or shell, the shape of a wall or pillar. Then if one returns to this scene after a few days, he will discover that the wooden form has been removed, and the gruel has solidified to a hard, stone-like mass, which conforms in shape to the mold in which it was cast. This artificial stone structure is called concrete, and the gray powder, the substance which binds sand and gravel together, is Portland cement.

This Portland cement which today is used so extensively in the construction of concrete buildings, roads, bridges, and dams is the result of hundreds, one might almost say thousands, of years of research and experimentation. Ever since man first started to build he has felt the need for some cementing material such as Portland cement to bind together the small stones or

other aggregate employed in construction, and for the purpose of giving walls and floors a smooth surface. The first cementing material ever used was apparently moistened clay, which was found to be plastic and to harden on drying. The Assyrians and Babylonians are known to have used moistened clay in construction, and the walls of ancient Egyptian buildings were made of bricks dried in the sun and cemented together with moist clay. Massive structures, however, such as the Pyramids, which were made of heavy blocks of stone, required a more durable cementing material which was harder after setting. The Egyptians carried out experiments which led to the discovery that the mineral gypsum, when calcined or burned[1], and moistened with water, made an excellent cementing material. This cement, now known as plaster of Paris, they mixed with sand to form the mortar used in the construction of the Pyramids. This discovery of the Egyptians that heat applied to certain rock minerals produced cementing substances was later employed by the Greeks, who produced lime by burning limestone or marble. With lime as a base, the Greeks made a number of very satisfactory mortars by admixture with sand or with sand and volcanic earths (pozzolana). These pozzolana mortars, which were found to resist the action of both fresh and salt water, were further developed by the Romans, who brought both the production and use of cements to great perfection, as is shown by the many examples of their work which still exist. These Roman cements were in many respects similar to the present-day Portland cement.

The quality of building cements declined with the decline of Rome. Even the art of lime burning was

[1]The term "burned" as used in the literature on the production of limes and cements does not mean that rock material took fire, but simply that it was heated to a high temperature.

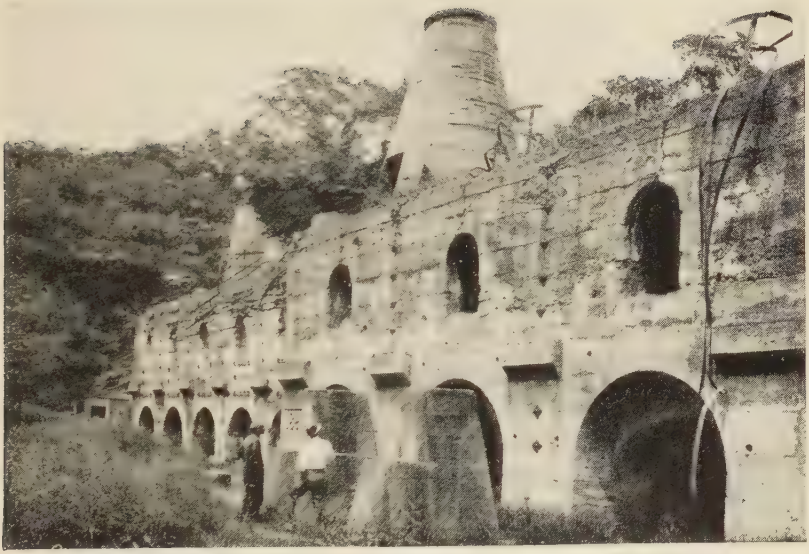
almost lost, and it was not until about the middle of the eighteenth century that interest in the development of building cements was again revived.

The Beginning of the Modern Cement Industry

In 1756 John Smeaton, an English engineer, carried out some investigations which may be considered the starting point in the development of the modern cement industry. Smeaton had been employed by Parliament to build a lighthouse upon a group of partially exposed rocks in the English Channel. Two wooden structures had previously been built and each had experienced a comparatively short life, but Smeaton attacked the problem, determined to build a structure which would weather the fiercest storms of the channel. One of the great difficulties he had to overcome was the failure of ordinary lime mortar to harden under water; and in order that his foundation should be firm it was necessary to find some mortar which would meet this requirement. To this end he undertook a series of investigations of lime mortars, the result of which was the discovery that a clayey limestone, when burned, produced a mortar which would not only harden better in air than ordinary lime but would also harden under water. Such a clayey limestone Smeaton found in Cornwall and by burning this stone he made hydraulic lime, which, when mixed with pozzolana, produced the satisfactory mortar used in the construction of the Eddystone lighthouse. This cement, while undoubtedly an excellent structural material, has never been widely used, because pozzolana is found only in a few volcanic regions, notably Italy, where it was once used in the making of the famous old Roman cements.

The scarcity of pozzolana led to further investigations to determine the possibility of making a satisfactory water cement without this ingredient, and as a result various processes for the manufacture of artificial Roman cements were patented. These so-called cements were really hydraulic limes, similar to that prepared by Smeaton, though they were made by burning limestone containing a rather higher percentage of clay. It was from one of these hydraulic limes, patented in 1824 by Joseph Aspdin, an English bricklayer, that Portland cement derives its name. Aspdin took out a patent for the manufacture of an improved cement, which he called Portland cement because, after hardening, it looked like Portland stone, a famous English building stone. This cement was made by heating together an intimate mixture of limestone and clay at the temperature ordinarily employed in the production of lime. The cement thus produced was not what is now known as Portland cement, the temperature of burning not being sufficiently high. This defect, however, soon became obvious; and the value of burning to a temperature sufficient to cause incipient fusion was discovered in 1825.

While the superiority of the cements thus made by partial fusion of the raw materials was soon recognized, the knowledge of why fusion is essential has but recently been discovered. We now know that there are certain definite chemical compounds of lime and silica which impart to Portland cement its most valuable properties; and that it requires extremely high temperatures to produce these compounds from limestone and clay. In spite of the lack of scientific knowledge during the early stages of the development of the Portland cement industry, the proper proportions of limestone and clay were discovered by burning various



Courtesy, Portland Cement Association

Cement Kilns of Yesterday

mixtures and testing the properties of the cements thus obtained.

Portland Cement in the United States

At first the English and later the German process produced cement which was the standard of quality; today, however, the best Portland cement is undoubtedly made in America. This has been brought about by the application of chemistry to the control of the manufacturing process, and by improvements in the mechanical appliances of the industry, which have been developed largely in this country, and which gradually increased the quality and uniformity of the product.

The manufacture of Portland cement in the United States dates from 1872, when David O. Saylor, a cement manufacturer of eastern Pennsylvania, undertook its production. The first method employed was rather crude. The raw materials—limestone and shale (clay which has turned to stone), or limestone and cement rock, a clayey limestone—were mixed in proportions based on experience and judgment, ground to a fine powder, mixed with water, and molded into bricks which were burned in an upright kiln, similar to that employed for the burning of lime. A coal fire was maintained at the bottom of the kiln and the bricks of raw mix loaded in at the top. The bricks became gradually heated as they passed down through the kiln and finally were fused as they passed through the zone of burning coal. The cement clinker thus produced was not always uniformly burned and it was often necessary to separate by hand the good from the improperly burned clinker. The good clinker was then ground to a fine powder and tested for its cementing qualities. Every step in this process as carried out in the early

days of the manufacture of Portland cement in America was a matter of uncertainty. As a result, the quality of the product was uncertain, and its use was limited.

Gradually the difficulties encountered in the production of a uniform product were overcome. The chemist was called in to analyze the raw materials. He found that the essential substances required in the raw materials were the mineral oxides lime, alumina, and silica, and that these mineral oxides must be present in certain, rather definite proportion in order to produce a uniform cement of good quality. He also found that fine grinding and uniform mixing of the raw materials were essential, and that there was a minimum burning temperature below which good Portland cement could not be produced. With these requirements as a basis, the chemist, with the assistance of engineers, developed the necessary mechanical appliances for producing a uniform cement of good quality.

These developments required many years of research and experimentation; but a still longer time was required to establish the superiority of American-made Portland cement. From the very beginning the Portland cement industry of the United States had to contend with keen competition, not only from established brands of European Portland cement, but also from the so-called Roman cements manufactured in the United States. In 1895, the domestic Portland cement industry, then twenty-three years old, was producing about one million barrels a year, less than one-third of the Portland cement used in the United States. Five years later, however, the industry began to reap the rewards of its painstaking research and development; domestic production of Portland cement was over eight million barrels a year, which was greater than

either imports or domestic production of the Roman or natural cements. Since that time the production of American Portland cement has increased by leaps and bounds, while its competitors have almost disappeared from the market. At the present time there are over one hundred and thirty operating plants, scattered throughout the country, with an annual production capacity of about one hundred and fifty million barrels (twenty-eight million tons) of Portland cement. The production of this vast quantity of cement requires that forty-eight million tons of raw materials be put through varied and exacting manufacturing processes.

Raw Materials for Cement Manufacture

Although over 75 per cent of the earth's crust for a depth of ten miles is made up of lime, alumina, and silica, which are necessary for the production of Portland cement, only a small percentage of this great mass of rock and earth consists of mineral deposits which are suitable raw materials. Ordinarily two raw materials are employed, one of which consists largely of calcium carbonate and the other of aluminium silicates. The most typical materials answering to this description are limestone and clay, both of which occur in a number of varieties in large deposits of uniform composition at, or near, the surface of the earth. At times deposits of clayey limestone, known as cement rock, are found which contain all three of the essential mineral oxides in nearly the proportions required for the production of Portland cement; but usually either limestone or clay has to be added to obtain the desired composition. Other raw materials sometimes used are blast furnace slag and limestone. However, any combination of raw materials containing lime, alumina, and

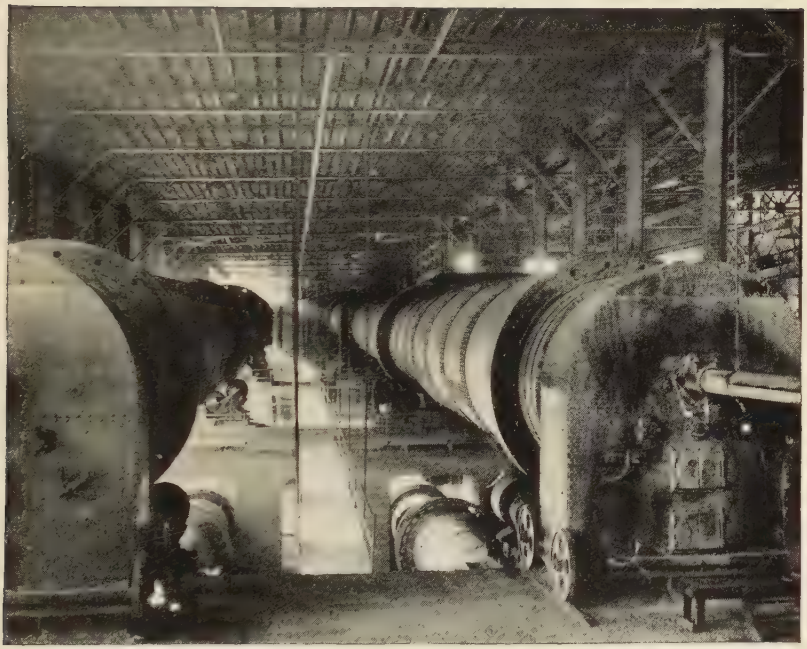
silica in suitable form and in the proper proportions may be used.

Plants for the manufacture of Portland cement are always located near the source of raw materials, not only because of the great quantity of raw materials that has to be handled but also because for every ton of cement produced about 1.7 tons of raw materials are required. It is also essential that the source of raw materials be sufficiently extensive to last for a long period of years and that its composition be reasonably uniform.

Process of Manufacture

The first step in the manufacturing process involves gathering the raw materials. The manner in which this operation is carried out varies with the nature of the materials. If rock materials, such as cement rock and limestone, are used they are quarried by blasting; whereas soft, wet materials, such as marl and clayey mud, are gathered by dredging operations. In the first case the raw materials are usually kept dry throughout subsequent operations, while in the latter case they are kept in a fluid condition until dried out in the kiln when the cement is burned.

In the dry process the cement rock and limestone, whose chemical composition has previously been determined, are loaded by steam shovels into cars and transported to the mill. At the mill each rock material is separately broken up in crushers and conveyed to storage bins located over scales where the proper proportions are weighed out and mixed. The mixture is then passed successively through crushers, driers for removing moisture, another series of crushers which further reduce the size of the rocks, and finally through



Courtesy, Portland Cement Association.

Modern Rotary Cement Kilns.

pulverizers which reduce the mix to a fine powder, which is then ready to be burned.

In the wet process the raw materials, if they are sufficiently fluid, may be pumped through pipes to the mill where they are separately ground in a wet condition, and then stored in tanks which are constantly agitated to keep the finely divided particles from settling. Careful chemical analyses are then made of the fluid contents of each tank and measured portions of the fluid marl and clay are piped to a mixing tank, from which the mixture is in turn piped to the kilns.

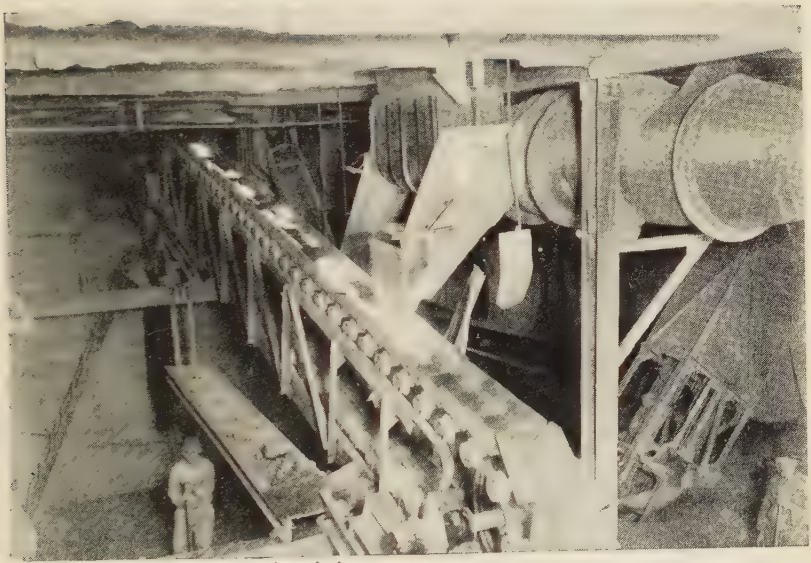
These two methods of procedure for gathering and proportioning the raw materials are not necessarily always carried out as described. It may be at times that only one of the raw materials is found in a fluid deposit that can be piped to the mill, or again it may be that both raw materials are received at the mill dry, and are then mixed with water for grinding and proportioning.

The wet process has certain advantages over the dry process in that it is a cleaner method of procedure and eliminates dust losses in the grinding operations, but of course considerable expense is necessarily involved in drying the wet mix or slurry, as it is called, before it is burned. After the mix reaches the kiln there is but little difference between the wet and dry processes and the resulting cement is essentially the same.

The burning of the raw mix is carried out in a rotary kiln, the action of which is continuous, the raw mix entering at one end and the cement clinker passing out the other. These kilns are cylindrical, ranging from one hundred to two hundred and fifty feet in length and six to ten feet in diameter, and are built up of steel plates lined with highly refractory material; they are supported in a slightly inclined position by friction

rollers and are slowly rotated. The fuel used is either pulverized coal, fuel oil, or gas which is blown by compressed air into the lower end of the kiln, thus securing thorough combustion and producing a flame thirty to forty feet in length. This arrangement insures the maintenance of a high temperature at the lower end of the kiln, so that the raw material passing down encounters a continually increasing temperature. The changes taking place in the progress of the material through the kiln may be divided into three stages: in the first the material is thoroughly dried, in the second all organic matter is destroyed and the carbon dioxide (gas) of the calcium carbonate is expelled, while the third is the chemical reaction between the lime, alumina, and silica to form the clinker. The time of passage through the kiln is about one and one-half to two hours and the maximum temperature is about 1425° C. The clinker, in the form of granules varying in size from that of a pea to that of a large marble, is a partially fused mass of the chemical substances formed by the reactions occurring in the third stage, and when ground to a fine powder it constitutes the Portland cement of commerce. It is usual, however, to mix with the clinker before it is ground a small portion of gypsum, the purpose of which is to regulate the time of setting of the cement when mixed with water.

It has been stated that Portland cement clinker is the result of chemical combination of the three oxides, lime, alumina, and silica; but besides these three—which are the essential components—two others, magnesia and iron oxide, always occur to some extent in commercial cement. According to Richard K. Meade, cements of good quality usually fall within the following limits of composition:



Courtesy, Portland Cement Association.

Continuous Discharge of Hot Cement Clinker.

	Limits Per cent	Average Per cent
Lime	60-64.5	62.0
Silica	20-24.0	22.0
Alumina	5- 9.0	7.5
Magnesia	1- 4.0	2.5
Iron oxide	2- 4.0	2.5
Sulfur trioxide	1- 1.75	1.5

This tabulation is the result of chemical analysis which gives the percentage of each component present, but does not indicate the nature of the chemical combinations of the components as they occur in Portland cement.

Chemical Constituents of Portland Cement

The chemical constituents of Portland cement are largely compounds of lime, alumina, and silica, of which tricalcic silicate ($3CaO.SiO_2$), dicalcic silicate ($2CaO.SiO_2$), and tricalcic aluminate ($3CaO.Al_2O_3$) are the major constituents, and uncombined lime (CaO) and the compound $5CaO.3Al_2O_3$ are minor constituents. The compounds formed by the oxides of iron, magnesium, and the alkalies which are always present in cement in small percentages, are a matter of some uncertainty. It would appear, however, that the iron oxide is present to some extent as dicalcic ferrite ($2CaO.Fe_2O_3$), and that the alkalies and magnesia are largely present as glass.

The major constituents—tricalcic silicate, dicalcic silicate, and tricalcic aluminate—which impart to Portland cement its valuable cementing properties, were determined as the result of extensive research, involving the preparation and study of all compounds formed when lime, alumina, and silica are fused together in various proportions. Each of these compounds was

found to have optical properties peculiar to itself which serve to distinguish it from the rest when mixtures are subjected to microscopic examination. Data on the several characteristic optical and crystallographic properties were obtained by a microscopic study of each compound by itself. Since these values for the individual compounds are constant in all fused mixtures of lime, alumina, and silica, it was possible to determine the compounds present in Portland cement clinker by microscopic examination. This microscopic examination also revealed that the three compounds, tricalcic silicate, dicalcic silicate, and tricalcic aluminate, comprise about 90 per cent of Portland cement.

A knowledge of the chemical compounds present in Portland cement is of importance not only in its relation to the manufacture of cement, but also in connection with the use of cement when it is mixed with water and hardens.

When Portland cement is burned the compounds of lime, alumina, and silica are formed with great rapidity at the maximum temperature, but they are formed always in a definite and orderly manner. The first of the silicates formed is dicalcic silicate; subsequently this compound unites with more lime to form tricalcic silicate. It is this reaction which requires that the temperature of burning be sufficiently high to fuse the raw mix. It is also essential that this reaction go practically to completion for the production of good cement, since tricalcic silicate is the most important constituent of Portland cement. Of the aluminates the compound $5CaO.3Al_2O_3$ is first formed. This compound subsequently unites with lime to form tricalcic aluminate. While it is desirable that this reaction go to completion, it is not necessary for the production of a sound cement.

The Hardening of Cement

The importance of properly carrying out these reactions, particularly the reaction which results in the formation of tricalcic silicate, is more clearly understood if one considers the cementing value of the constituents of Portland cement, and their relation to the changes which take place when Portland cement is mixed with water and hardens.

When Portland cement is finely pulverized and mixed with water, a hard mass is formed by chemical action between the water and the constituents of the cement. The first change undergone by the cement mortar in passing from a plastic to a solid state is called "setting," and requires only a few hours. After the mortar has set, there is a gradual increase in the strength of the mass, and the cement is said to harden. It sometimes requires a year's time for a cement to acquire its full strength.

While there is still much to be learned as to the chemistry of the hardening of Portland cement, sufficient data on the hydration (reaction with water) of the individual major constituents have been obtained to enable us to account for this gradual hardening and increase in strength, and to indicate the relative value of these constituents as cementing materials.

Each of the major constituents sets and hardens in a different manner. When tricalcic aluminate is mixed with water a gelatinous hydrated material is first formed, which sets and hardens very rapidly. The compound tricalcic silicate, when mixed with water, also sets and hardens rather rapidly. In both cases the setting and hardening are due to the formation of a gelatinous hydrated material which cements together the individual grains. Dicalcic silicate reacts very

slowly with water, and it is only after a long period of time that sufficient gelatinous material is formed to cement the grains of this compound and so form a solid mass.

The gelatinous material formed by the action of water on the constituents of cement does in time, no doubt, crystallize to some extent. From the available data it would appear that the crystals formed are calcium hydrate and some crystalline hydrate derived from tricalcic aluminate. Apparently no crystalline hydrate of the calcium silicates is formed. The gelatinous mixture of lime and silica first formed seems ultimately to become a mixture of gelatinous silica and crystalline lime hydrate.

It will therefore be seen that the setting and hardening of Portland cement involves the formation of a gelatinous material which subsequently partially crystallizes; that the initial set is probably due to the hydration of tricalcium aluminate; that the hardness and cohesive strength at first are due to the cementing action of gelatinous material produced by the hydration of this aluminate and of the tricalcic silicate; and that the gradual increase in strength is due to the further hydration of these two compounds, together with the hydration of the dicalcic silicate.

Of the three compounds which thus take part in the setting and hardening of Portland cement, the tricalcic silicate is the best cementing constituent; that is, this compound is the only one of the three which when mixed with water will set and harden within a reasonable time to form a mass which in hardness and strength is comparable to Portland cement. The dicalcic silicate requires too long a time to set and harden to be in itself a valuable cementing material. The tricalcic aluminate, while it sets and hardens with great

rapidity, is rather soluble in water and is not particularly strong or durable.

From this it is evident that tricalcic silicate is the most essential constituent of Portland cement, its cementing value being apparently due to the fact that it readily releases gelatinous silica when mixed with water. There are a number of other substances which, when mixed with water, release this fundamental cementing material, gelatinous silica; but none of these other substances are capable of imparting to a cement the characteristics required in modern construction. Dicalcic silicate is one of these substances. It sets and hardens when mixed with water but gelatinous silica forms so slowly that several months are required for molded specimens to develop any appreciable strength and hardness. A cement requiring such a long time to set and harden would seriously delay the erection of concrete structures. A modern reinforced concrete office building, instead of being erected in several months, would probably require several years, since it would be necessary to wait for each bit of concrete construction to develop sufficient strength to serve as a foundation for further construction. The ultimate strength and durability of a concrete in which dicalcic silicate was the essential cement material would, however, be as great or greater than a concrete in which tricalcic silicate was the cementing material.

The ancient Roman cement previously discussed belongs to the class of cements which develop strength and durability slowly, by the slow release of gelatinous silica. This cement was a mixture of lime and pozzolana, a material of volcanic origin containing silicates. When mixed with water, the action of lime in solution slowly released gelatinous silica from the pozzolana. The present excellent condition of many of these Ro-

man mortar structures is sufficient evidence of their strength and durability.

It was undoubtedly as true of Roman cements as it is of modern Portland cement, that the strength and durability developed in mortar and concrete are dependent not only on the quality of the cement but also on the way the mortar and concrete are made. One often sees a cement sidewalk or other concrete structure which has disintegrated. If the reason for this condition were determined, it would undoubtedly be found, in the majority of cases, that the fault lay with the method of mixing the concrete and not in the quality of the cement.

Extensive researches have been carried out to determine the best method of incorporating the ingredients of concrete, the nature of the aggregate, sand, gravel, etc., to be used, and the proportions of cement, water, and aggregate, in order that the resulting artificial rock mass shall develop the greatest strength. A great deal has been accomplished as a result of this research, as is evidenced by the fact that one may now proceed to the construction of concrete roads, bridges, dams, and buildings, with reasonable assurance that if proper methods are employed a permanent structure will result.

The Field for Research

Although the cement now manufactured is a highly satisfactory structural material, there still remains a field for research and improvement. Until recently the knowledge of how to use Portland cement in concrete making was far behind the developments in its manufacture. Even now there is much to be learned in regard to the factors which govern the strength and

quality of cement structures. In connection with the manufacture of Portland cement there are several interesting research problems which deserve serious consideration. These problems are in a way speculations, but they are based on our present knowledge of the constitution of Portland cement clinker and of the changes which take place when the finished cement is mixed with water and hardens.

It will be remembered that the most important constituent of Portland cement is tricalcic silicate and that its value as a cementing material is due to the readiness with which it liberates gelatinous silica when mixed with water. This compound makes up only about 20 to 30 per cent of an average Portland cement clinker. One would expect, therefore, that any improvement in the manufacturing process which would increase this percentage would increase the cementing value of the resulting cement. This could be accomplished by increasing the lime content of the raw mix and increasing the temperature of burning so that more lime would react to form tricalcic silicate according to the equation $2CaO.SiO_2 + CaO = 3CaO.SiO_2$. Unfortunately the temperatures required for this purpose are such that it is not at present economically feasible to increase the percentage of tricalcic silicate in this way. Ultimately research will no doubt solve this problem.

Another interesting problem is concerned with methods of procedure for the rapid release of gelatinous silicate from compounds such as dicalcic silicate. This compound is much more readily produced than tricalcic silicate; it contains a higher percentage of silica, and when mixed with water produces a sound cement which should ultimately be as strong or stronger than tricalcic silicate cement. The problem

of hastening the setting of dicalcic silicate is up to the research chemist for solution.

Following out this line of thought, that gelatinous silica is the fundamental structural cementing material, the ideal cement should be a practically pure silica which would become gelatinous when mixed with water. Such a cement as this, when mixed with sand and gravel, should produce the ideal concrete, similar to the toughest sandstones found in nature, which are made up of grains of sand originally cemented together with gelatinous silica, gradually deposited from solution onto the grains of sand, and subsequently hardening.

Reading References

Dancaster, E. A. Limes and Cements. London, 1916.
Desch, C. H. Chemistry and Testing of Cement. London, 1911.
Eckel, E. C. Cements, Limes and Plasters. New York, 1913.
Meade, R. K. Portland Cement. Easton, 1925.

CHAPTER XVI

CHEMISTRY, RADIO, AND INCANDESCENT LAMPS

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Long before wireless communication was more than a fantastic dream, scientists were working hard to develop incandescent lamps, unaware that the results of their labors would sometime be applied to the task of communication across seas and continents. For the success of radio communication has been largely dependent on the development of radio tubes, and these tubes have been the direct outgrowth of the high vacuum incandescent filament lamp.

This chapter attempts to show the vital importance of chemistry in the perfection and production of such lamps and tubes. The electrical engineering side of radio will not be touched upon here because, though chemistry has served in that field (as, for instance, in the development of pure, highly conducting copper, of alloys, of porcelains, insulation, and dielectrics), these phases have been described more or less elsewhere in this or the previous volume.

In 1879, Edison in America and Swan in England produced nearly simultaneously the first practical incandescent lamps, and so made possible the use of small units in electrical lighting. The phenomenal growth of this system of lighting is an old story.

Development of Filaments

Edison experimented with platinum filaments but found carbon to be better. His early filaments were made from paper or cotton thread, but later he used bamboo fibers. These were heated to a high temperature in a furnace closed from the air and so were charred to threads of almost pure carbon. Somewhat later the carbon squirted filament was made. This was prepared by dissolving cotton in a suitable medium to form a viscid fluid which was squirted through fine openings into a hardening bath, usually of alcohol. These threads, after drying and baking, yielded smooth, even filaments much more uniform than the earlier types. A final improvement in carbon filaments was made when they were "metallized"; that is, flashed in gasoline vapor to form a dense smooth graphitic deposit on the surface from the decomposition of the hydrocarbon. Metallized filaments can be run longer at a given efficiency than any other type of carbon filament.

In 1905 Siemens made the first tantalum lamp. Tantalum lamps never became important commercially because the filaments quickly went to pieces when burned on alternating current, but they showed the potentialities of metal filaments. They were very soon superseded by the tungsten filament lamp. The very high melting point and low vapor pressure of tungsten make it the best material so far found for filaments. The higher the temperature of a filament, the larger the fraction of the consumed electrical energy which is converted to visible light, and the more nearly does this light match daylight in color. Tungsten filaments are operated at from 2100° to 2300° C. normally, whereas carbon filaments are run at about 1700° C.

Courtesy, General Electric Co.

The Mightiest and Tiniest Electric Lamps.

The large one is rated at one hundred thousand candlepower and is used in motion picture studio work. The small one is about a quarter of an inch in diameter and runs on one-fifth of a volt. It has been developed for use by physicians and surgeons.

Moreover, since the vapor pressure of tungsten is low at these temperatures, tungsten lamps can run a thousand hours or more before enough tungsten has evaporated to the bulb to blacken it seriously.

A great many processes for the production of tungsten filaments have been proposed. Many chemical reactions are involved in any of them. The one commonly in use is that known as the drawn-wire method. By this method metallic tungsten in the finely powdered form is first prepared. This means that the ore, carrying tungsten usually as the oxide or as calcium tungstate, must first be purified by repeated solution in caustic soda or ammonia and precipitation with hydrochloric acid to obtain pure tungstic oxide powder. This oxide is then reduced to the metal by roasting in a current of hydrogen.

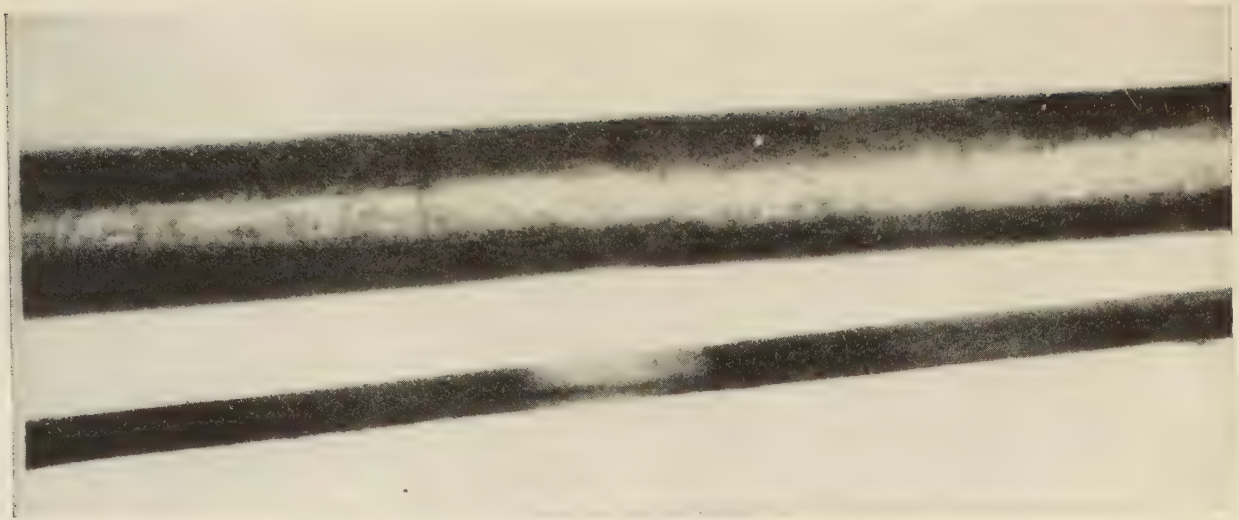
Because the melting point of tungsten is so high (3380° C.), it is not possible to melt the tungsten powder, except in an electric arc, and when so melted it freezes in brittle unworkable crystals; so it is submitted to the following treatment. First the powder is pressed into bars with hydraulic pressure. These are frail and porous. They are then heated in hydrogen in furnaces at about 1700° C., during which treatment they shrink and sinter together. They are then strong enough to be handled. The next step is to heat these bars by passing through them hundreds or thousands of amperes of current. This is done in an atmosphere of hydrogen under large iron hoods, and the current is high enough to heat the bars almost to the melting point of tungsten. After this treatment, the bar is practically a homogeneous piece of metal. It is then heated, swaged while hot, reheated, reswaged, and the process continued until it has been reduced to a long rod a little less than a millimeter in diameter.

This rod, or heavy wire, can then be reduced to filaments by repeated hot drawing through diamond dies. At each drawing the diameter can be reduced only a little, so that a set of forty or fifty dies is necessary to produce wire such as is used in the usual household size lamps and small tubes.

There are certain materials that are added to tungsten, usually when it is in the stage of tungstic oxide, or sometimes to the tungsten powder, to give the filaments desirable qualities. Among these materials is thoria (ThO^2), which has been used for many years in tungsten to prevent the development of very large grains or crystals in the filament during use, since such large grain structure makes the filament fragile.

Electron Emission

While Edison was working to perfect his carbon lamp, he observed that "electricity" would leak from the negative end of one of his hot filaments to a wire or plate that was more positive. This "Edison effect" suggested many experiments and was the basis of the work which finally led to the development of the radio tube or valve. We now know that it is electrons which are given off by the hot filament and travel to the positive plate. In 1905 Fleming, an engineer long connected with the Edison and Swan Lighting Company in London, put out the first vacuum tube containing two electrodes and applicable to detection of radio signals. Two years later the first three-electrode tube was invented by de Forrest for use as a receiver. These tubes were "soft," that is, contained some gas. In fact, gas was at that time considered necessary because electron emission was supposed to be due to a reaction between the gas and the material of the filament. But



Courtesy, General Electric Co.

The Size of a Wire, Such as is Used in the "Peanut Tube," is Here Shown in Comparison With a Human Hair. The Smaller One is the Wire, the Larger the Hair.

in 1912 Langmuir completed his critical study of electron emission, showing that it was due not to chemical action but to the high temperature of the filament, and took place in a good vacuum as well as in gas. He established the conditions of emission and conduction in good vacuum as a result of which we have the whole "tron" family, the kenotron, pliotron, magnetron, radiotron, etc.—"tron" coming from the Greek word meaning empty. High-vacuum tubes will stand high voltage, but tubes containing gas are when the voltage is raised above very moderate values. Therefore, all high-power tubes are of the high-vacuum type.

It is now known that the more electropositive metals, such as caesium, calcium, and thorium, give off electrons more easily than other metals, such as tungsten or platinum. In fact, the two properties of contact potential (which marks a metal as more or less electropositive) and electron emission are very closely connected. The earliest Fleming valves were made up with carbon filaments, later tungsten was used, and today many of the filaments contain some material which increases their power of electron emission. By a fortunate chance, one of the best of these materials is the very thoria which had been used for so long for other reasons in lamp filaments. In addition to the question of intrinsic activity as emitters of electrons, many chemical factors must be considered. For instance, the questions of reaction with tungsten (or whatever metal is used as the chief materials of the filament), of alloying, and of ease of reduction, are all vital as well as the purely physical properties of diffusion, evaporation, brittleness, etc.

Another phase of the subject of materials added to increase electron emission is the extremely interesting one of the formation of monomolocular films. In 1917

and 1918 Langmuir showed that small amounts of oils on water formed films one molecule thick, and that gases adsorbed on the surfaces of solids also formed these monomolecular layers; that is, layers one molecule thick. This work led to an understanding of the phenomena of monomolecular layers of thorium and of alkali metals on tungsten filaments, formed when such filaments are given the proper treatment in the presence of the active material.

The method of production of the high-electron emission observed in the case of an active filament containing thoria is as follows. The filament is heated to a high temperature for a short time, so that a very small part of the thoria is reduced by the tungsten, with which it is in contact, to metallic thorium. The filament is then heated for a longer time at a moderate temperature (say, 1750° C.), during which time some of the metallic thorium travels to the surface of the filament from inside, and forms there a layer of thorium one atom deep, covering the surface. The electron emission increases as the surface of the filament becomes covered with thorium, and when the covering is complete the emission becomes constant. As long as the radio tube is good, this thorium layer is present on the surface of the filament. During this time some thorium evaporates, but is replaced by other atoms diffusing from inside the filament.

When the tube becomes "dead" it may be either because it has been run so long that the thorium has all diffused out and there is no further supply to keep the surface covered, or else because the filament has been run too hot, so that the layer on the surface has evaporated so fast that the supply coming from the interior of the filament has been inadequate to keep the surface covered. In either case the activity can be brought

Courtesy, General Electric Co.

Dr. Irving Langmuir Holding One of the Most Powerful Sending Tubes and One of the Smallest Receiving Tubes.

back by running the filament quite hot for a short time and then for some minutes at the normal current. There are, of course, other causes for a tube's going dead which cannot be taken up here.

In some tubes, such as the large ones used in transmission work, the filaments containing thoria are carbonized. This process is a chemical one. The filaments are run at a fairly high temperature in a vapor of some hydrocarbon, which is decomposed by the heat of the filament and deposits carbon on it. The carbon is absorbed by the incandescent tungsten and reacts with it forming a compound W_2C. Such filaments have the power of keeping their surface layers of thorium for a longer time. This is probably because the carbon helps to reduce the thoria to thorium and so increases the supply of the latter inside the filament.

Gases

Such a film of active material is exceedingly sensitive to certain gases. Even a pure tungsten filament suffers great reduction in efficiency if such gases as water vapor, oxygen, or nitrogen are present. Here again the phenomena of monomolecular films enter in, since the reduced emission may be due to a film on the filament of nitrogen or of oxygen which has combined with the tungsten or thorium. These compounds remain on the filament long enough before evaporating to act as a coating and prevent normal electron emission. If the voltage across the tube be above fifty volts, the heavier gases, if present, will also destroy the film of active material on the filament by "bombardment" with the positive ions of the gases. That is, the positive ions formed from the gas by the electrons which come from the filament are drawn to the filament. This they

strike with sufficient force to knock off minute particles of metal. In a lamp, bombardment then wears down the filament at the negative end to a smaller diameter. This means that the negative end runs hotter, so that more tungsten evaporates from it. Eventually, then, the filament burns out at this point.

In the manufacture of lamps it was found long ago that gases, particularly hydrogen and moisture, must be kept out because if they were present even in small amounts, the lamps either blackened very quickly or burned out prematurely. Different gases act in different ways.

Water vapor is a particularly vicious gas, as its action is cyclic. When this gas strikes the filament it forms atomic hydrogen and tungstic oxide. The latter evaporates to the bulb wall. At the temperature of the bulb, however, the atomic hydrogen can reduce tungstic oxide, forming water which can again attack the filament. By the repeated action of a small amount of water vapor the bulb wall becomes coated with a layer of tungsten which absorbs the light from the filament and greatly reduces the efficiency of the lamp.

Hydrogen in a lamp will form water in case any oxide is present. As there is apt to be a small amount of oxide on the leads and near the places where the filament and leads are welded together, this makes hydrogen almost as dangerous as water itself. Other gases act chiefly by bombardment.

Gas in Glass

It has been found that glass bulbs used for lamps or tubes will give off considerable quantities of gas if they are heated, and that even when cold these gases

Courtesy, General Electric Co.

Variety of Vacuum Tubes in Production in 1923.

All of These Tubes Have Been Developed Since the Beginning of the Great War.

come out of the glass into a vacuum slowly. Over 90 per cent of what is given off is water vapor, the rest being chiefly carbon dioxide and nitrogen. There are two ways of getting rid of these gases in a lamp. The first is to bake the lamp during the time it is being pumped out. The gases are evolved rapidly and pumped off so that after cooling the glass will tend rather to absorb moisture than to give it off. This baking is done in all lamp factories. The temperature varies from about 200° C. to much higher, depending on the kind of glass used in the bulbs and the length of time the baking is continued.

Gas Absorbers

The second method of removal is used quite generally in American factories, but very little abroad. It consists in putting into the lamp, before it is sealed off, a small amount of some substance that has an affinity for moisture. The most common materials used in lamps are red phosphorus and phosphoric anhydride (P_2O_5). The phosphorus is usually applied to the filament as a coating before it is put into the bulb. When the filament is flashed for the first time, the phosphorus is volatilized and apparently reacts in the vapor form with the gases given off in considerable volume by the hot filament. At any rate these gases disappear as the phosphorus deposits out on the bulb. Probably a considerable part of the phosphorus is converted to the oxide during this process. These materials are able to take up any moisture that may be evolved during the life of the lamp. It has been found that for radio tubes the reactive metals, such as calcium or magnesium, may be used to advantage to replace or to supplement the action of phosphorus. They are vaporized

onto the walls of the tube so that they present a large reaction surface. Naturally such metals cannot be used in lamps because they are not transparent.

In production of radio tubes additional precautions are taken to keep them gas free. The metal parts are heated to a red or even a white heat while the tube is connected to the vacuum pump. This is done either by heating the parts in the field of a high-frequency coil, the eddy currents induced producing immense quantities of heat; or by making them strongly positive to the filament, running the filament quite hot and producing heat at the anode by bombardment with electrons. Quantities of gas are evolved in such a heating, and are carried off by the pump. Metal parts are sometimes baked at high temperatures in vacuum or in hydrogen furnaces before they are built into the tubes. They may also be cleaned with chemicals or in an electrolytic bath. As new tubes containing new materials come into use, new methods of "de-gassing" are adopted. Work is progressing daily, giving us knowledge of different gas absorbers, or "getters" as they are called, of the amounts and kinds of gas they will take up, and of the effect of temperature on their capacity to hold gas. Apparently their physical state makes a difference too. For instance a solid piece of calcium is not so effective as the same calcium in vapor form or as a thin film. Some "getters" *ab*sorb gases, some *ad*sorb, and some react with them. Probably most getters do two or all of these things. Moreover, some metals, unless carefully treated beforehand, may contain very large amounts of gas, others very little, and different metals different gases. Our very "getters" may under exceptional conditions give off gas instead of taking it up. Much investigation needs to be made before we shall know all the conditions of gas evolution and its

prevention. There is one fortunate fact in our favor and that is that in any tube run with fifty volts or more there is a constant tendency for small quantities of gas to disappear. Apparently the gas under the influence of the voltage discharge is driven into the glass. Part of this gas can be reëvolved by heating, but part seems to be held permanently. This clean-up of gas is not yet thoroughly understood.

Conductivity of Glass vs. Composition

The kind of glass of which radio tubes are made is of importance, particularly that used in the stem where the wires (leading-in wires or leads) are sealed through. If glass of the wrong composition, too high in sodium or potash, is used it will act as a conductor, a poor one it is true, but often conducting enough current by electrolysis to cause the stems to crack. Testing of glasses of various compositions suitable for different types of tubes goes on continuously as part of the development of such tubes. Moreover, some glasses seem to form a conducting layer of whatever alkali metal is used in the tube so that current will leak from wire to wire across this metal film. The action by which such films are formed is not well understood —another field for research work.

So far nothing has been said of gas-filled lamps or tubes. When, instead of vacuum the bulbs are filled with gas, such as nitrogen or argon, a double complication is introduced. First, the purity of the gas must be assured by chemical cleansing and tests. Secondly, the action of the gas on the filament must have been determined. In gas-filled lamps nitrogen and argon are used because they do not attack the tungsten and do not exert too great a cooling effect on the filament. They

do, moreover, blanket the filament so as to reduce evaporation of the tungsten and also carry the tungsten that does evaporate to the upper parts of the bulb, where it can deposit without cutting down the efficiency of the lamp.

The tendency in radio appears at present to be away from gas-filled to high-vacuum devices, but there are already on the market gas-filled rectifier tubes and voltage-control tubes and one may expect a great diversity of such gas and vapor tubes in the near future.

There have been various forms of tubes or lamps put out from time to time which depend for their illuminating power on the glow of gases through which current is passing. Such are the well-known Moore tube and the neon glow lamp, including those ornamental ones containing metal letters surrounded by glowing gas. Anyone who has kept in touch with lamp development during the past decade views with interest these glow lamps, a distinct departure from the hot filament type of illuminant. The ideal lamp is, of course, one radiating all its energy as visible light, and none as heat or ultra-violet radiation. The most hopeful directions in which to search for this ideal appear now to be in the gas glows and the phosphorescent or fluorescent glows. This means an entirely new series of researches and undoubtedly the chemist, provided he view himself not as a chemist only but rather as an investigator, will be instrumental in bringing us great benefit by his work in these fields.

Reading References

Coursey, Philip B. Telephony without Wires.
Dyer and Martin. Edison, His Life and Inventions.
Fleming, A. Principles of Electric Wave Telegraphy.
Gaster and Dow. Modern Illuminants and Illuminating Engineering.
Luckiesh, M. Artificial Light.

Martin and Coles. The Story of Electricity.
Morecroft. Principles of Radio Communication.
Schroeder, Henry. History of Electric Light. Publication No. 2717 of the Smithsonian Miscellaneous Collections.
Stanley, R. Wireless Telegraphy.

CHAPTER XVII

RAILROAD CHEMISTRY

WM. M. BABB

Consulting Chemist, Union Pacific System

What does a chemist do for a railroad? This question is frequently asked by laymen when they learn that the railroads of the country employ chemists. Half of us do not know how the other half lives, and it is for this reason that the application of chemistry to railroading may be of interest to the reader of this volume.

A railroad represents a great industrial community and while its primary function is transportation, it is in a way a great manufacturing concern. The railroads of the country employ nearly two million men and their property has a physical valuation of approximately twenty billion dollars. The purchases of materials and equipment for the railroads of the country amount annually to about $1,340,000,000. Their great shops for the upkeep of the equipment may well be compared with large manufacturing establishments. Therefore, when we consider that the steel mills, the locomotive works, the paint manufacturers, and nearly all the producers of the things used by the railways, maintain a staff of chemists for the control of their products, it is clear that the railroads, which are such large purchasers and users of these products, can profitably employ technical men with chemical training to control

Courtesy, Union Pacific System.

Modern Locomotive Owned by the Union Pacific System, in Which Special Alloy Steels Are Extensively Used. This Engine, the Latest Development in Large Power, Requires Good Oil, Good Coal and Good Water.

the quality of these purchases and to assist in their protection and maintenance after they are put in service.

In the early days of railroading, so much attention was given to the construction of new lines which ultimately made up the great network of railways of this country, that little attention was given to the quality of the materials used. However, as long ago as 1875, the Pennsylvania Railroad, recognizing the importance of controlling the quality of purchases, decided to establish a laboratory to handle the physical and chemical testing of materials purchased and used by this great railroad. The officials of the road therefore selected Dr. Charles B. Dudley, a graduate of Yale University, as chief chemist and he started his work on November 10, 1875. He organized a new department of chemistry, for which no precedent existed and gave the remainder of his life to this service. He proved the practical value of this work and it is largely due to his efforts and results that such a department has become a permanent feature in the organization of a railroad. The other great railway systems of the country established similar positions several years later.

Today there is no railway of great importance that does not have a department employing a number of trained men under the direction of a chief chemist or an engineer of tests, to handle the checking of materials and to study the various problems of chemistry which constantly arise in such a great industrial organization.

The Scope of Railroad Chemistry

The large locomotive of today costs from sixty thousand to seventy thousand dollars. In the make-up of

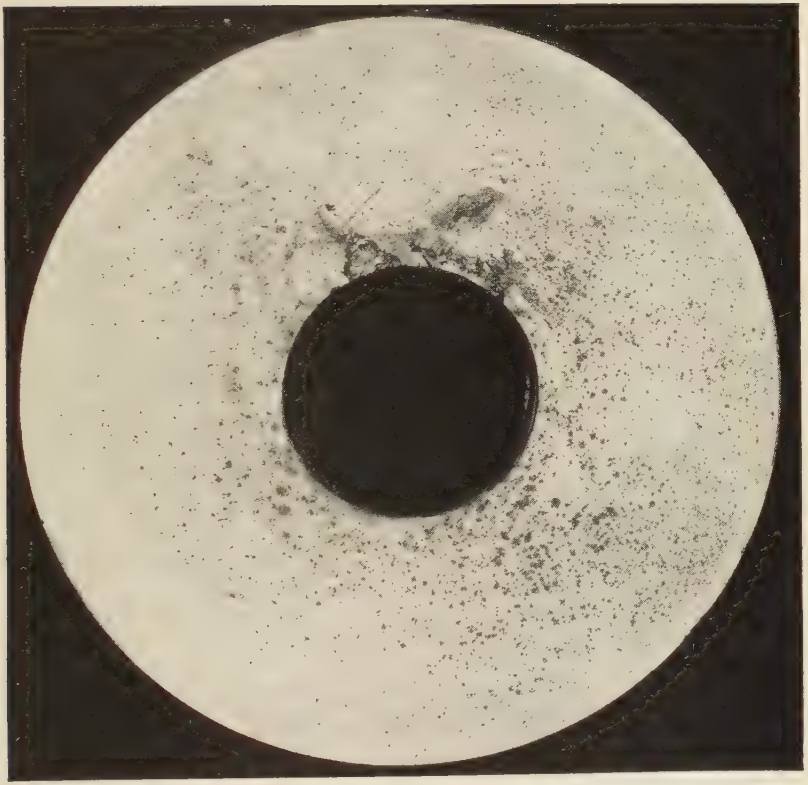
this great power plant there is a variety of metals, including special alloy steels, brasses, bronzes, babbitt metals, lead, and various grades of steel and iron. Some of the railroads own several thousand of these locomotives and it is necessary to study constantly the materials used in their construction in order to maintain efficiency and protect the thousands of passengers from accidents which might result by the failure of some part of these machines. In the maintenance of the locomotive and the cars making up a train, it is necessary to know the quality of all the materials used.

Paints and Varnishes

The painting of railway equipment and structures is an important problem in maintenance. The proper protection of the surface of railway property is not only good economy, but the appearance of well painted equipment and structures makes a favorable impression upon the traveling public. The use of poor paint is expensive at any price, as the labor cost for its application is much greater than the cost of the material itself. It is therefore necessary that the most serviceable material be purchased for this work.

All paints and varnishes received by the railroad company are bought under specifications and are subjected to laboratory examination, including chemical analysis and physical test. Practical service tests are made under the direction of the chemist to determine the kind of paint or varnish best suited for the service.

Paints intended for special purposes or for which special claims are made are given accelerated service tests and in this way many products for which false or mistaken claims are made, are eliminated. There has been great progress in this industry in recent years,



Courtesy, Union Pacific System.

Etched Cross Section of 12-inch Locomotive Driving Axle Which Failed Because of Defective Material.

both in the manufacture of the material and in methods of application. It offers a field which fully justifies the attention now being given to it by the railway chemical laboratories. The new class of cellulose lacquer finishes which has been developed in recent years is already being used to a considerable extent in railway service and it is possible that this new system of painting may entirely supplant the older varnish methods of finishing railway coaches. In this line there are several problems to be worked out and it is probable that within a short time a number of railways will have arrived at a decision as to the practicability of this new chemical finish which has already proved its worth on automobiles.

The Water Problem

The water problem constitutes the largest single chemical problem of a railroad. This statement may surprise the lay reader since he considers water one of the simplest and most abundant of all chemical compounds. Surely water is abundant, but nature rarely provides this chemical in its pure state.

Natural waters may contain a number of other chemicals in solution. These include silica, compounds of iron and alumina, calcium bicarbonate, magnesium bicarbonate, calcium sulfate, magnesium sulfate, sodium bicarbonate, sodium sulfate, sodium chloride, sodium nitrate, small amounts of potassium salts, organic matter, dissolved oxygen, carbon dioxide, hydrogen sulfide, and some other minor impurities.

The railroads have water supplies located at intervals of twenty to thirty miles and these supplies may be quite different in chemical composition, so that the same locomotive boiler which has to take a number of

these supplies may have a variety of reactions going on within it, which may injure the metal or may interfere with the successful operation of the engine.

Removal of Boiler Scale

Some of the compounds here mentioned are contained in natural waters in considerable quantity and some of them, such as calcium and magnesium salts, are thrown out of solution at the temperature of the boiler water and this precipitate attaches itself to the tubes, forming a heavy hard scale. Sometimes this scale very closely resembles a piece of porcelain or pottery and sometimes it builds a layer of this kind of considerable thickness.

Now this deposit is a very fine insulating medium and it is easy to understand that it will require much more fuel to heat the water in the boiler through this layer of stone than it will through the clean steel of a new boiler tube. It has been determined, with some degree of accuracy, that a representative boiler scale, one-eighth inch thick, will require approximately 15 per cent more fuel than a clean boiler. In addition to this loss in fuel, the increased heat required injures the boiler tubes, sometimes burning them so that they deteriorate rapidly when the scale cracks and the water reaches the hot tube. It is therefore evident that the removal of this scale is of great importance to the railroad.

The American Railway Engineering Association has tried to estimate the cost of boiler scale. Taking all factors into consideration, their calculation indicates that every pound of scale kept out of the boiler saves the railroad company thirteen cents. When we consider that an engine running five hundred to six hun-

Courtesy, Union Pacific System.

Section of Feed-Water Pipe Showing Scale Deposited in Eight Months.

dred miles, with a passenger train, will evaporate fifty thousand gallons of water and that it is not unusual for western waters to contain from two to four pounds of scale-forming solids per thousand gallons of water, it is easy to calculate how much it means to keep these harmful ingredients out of the boiler.

The removal of scale-forming solids is accomplished by chemical treatment of the water in what is commonly known as a water softener. The illustration will give some idea of the appearance of one of these plants. In some cases where it is not practical to install water softeners, either for financial or other reasons, the formation of scale is relieved by the addition to the water of chemical mixtures known as boiler compounds. These compounds have a tendency to throw down the incrusting matter as a soft sludge and it is removed from the boiler by blowing off.

Prevention of Corrosion

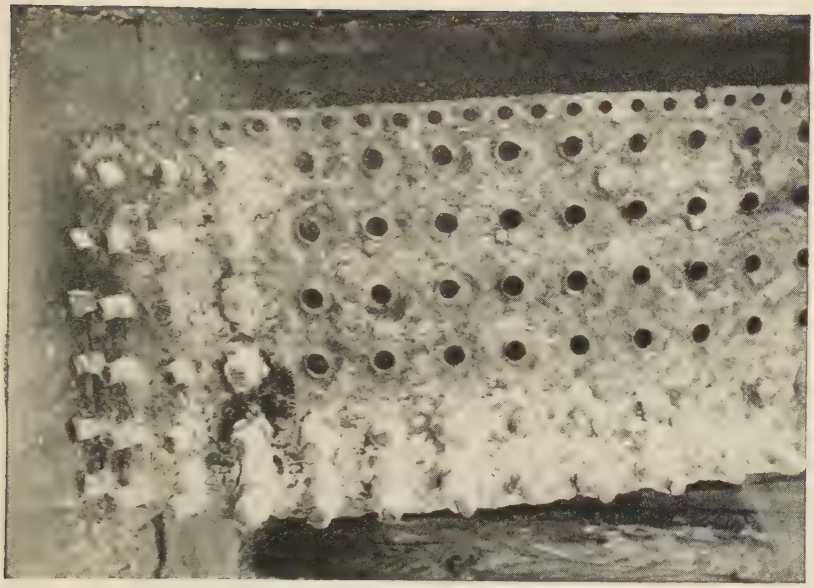
Besides the scale-forming salts in natural waters, some of these waters contain compounds which cause corrosion. One of the greatest sinners in this class is dissolved oxygen which we rarely think of as a harmful ingredient but rather a beneficial one. This element in solution in the water has an effect similar to its presence in moist air when a piece of steel is left out in the weather. All are familiar with the rusting of iron and steel when it is exposed to ordinary weather conditions. Now when this steel forms the tubes of a boiler, the dissolved oxygen, together with the salts in solution, works much more rapidly because of the high temperature of the boiler (about 380° F.) and the great pressure to which it is subjected.

It costs approximately two thousand dollars to re-

place a set of boiler tubes in one of the modern locomotives. Some waters actually used on our railroads have been so corrosive as to make it necessary to replace a set of these flues within six months. It is therefore evident that it is of great value to eliminate such waters or to improve them by treatment until the severe corrosive condition does not exist. The Government allows the railroads to run an engine for four years without replacing the flues. It is, however, unusual to find a condition so good that it is possible to use the flues to this limit. Engines are usually shopped for general overhauling at periods varying from twelve to eighteen months, the engines having run from seventy-five thousand to two hundred thousand miles, depending upon the service in which they are engaged. At such times the flues are removed and examined and if their condition is satisfactory they are reset to be run till another shopping.

The chemist is constantly at work devising means of increasing the life of this material. The locomotive firebox is subjected to the same corrosive conditions and this is another source of expense which the work of the chemist helps to reduce.

There are still other difficulties which some of these compounds in natural waters produce. One of the most disagreeable ones is the property that causes the engine to foam. After precipitation of some of the material which is insoluble at boiler temperatures and after the concentration of soluble salts is increased by evaporation, there is a tendency for boilers to develop a foaming condition, which, in the case of sudden starts or heavy pulls, causes some of the water to pass over into the cylinders. This reduces the efficiency in the cylinder on account of the wet steam and destroys the lubrication. When this condition occurs, it sometimes



Courtesy, Union Pacific System.

Section of Fire-Box Sheet Showing the Effect of Corrosion and Scale in Bad Water District.

results in a complete failure of the engine. This is not only an exaremely expensive occurrence but it prevents trains from being on time, which is considered by the railway management as a crime. The chemist is therefore called upon to prevent the occurrence of such conditions and accomplishes this by the addition of chemical mixtures to the boiler water. It is really a problem in physical chemistry and one which has been very successfully taken care of by the chemical engineer.

The importance of the water problem is due to the large savings that may be effected in locomotive maintenance by chemical treatment and the improvement in the service of locomotives. An engine failure is a very serious matter and the proper handling of water supplies has been one of the greatest factors on the American railways in reducing the number of engine failures.

Drinking Water

The U. S. Public Health Service exercises control over the sanitary condition of drinking water furnished to passengers on trains engaged in interstate traffic. All water supplies used for such purposes must pass inspection annually in the field by a sanitary engineer representing the Public Health Service and must pass sanitary examination in the laboratory of the State Board of Health. It is therefore necessary for the chemical department of a railroad to make a careful check on the chemical and bacteriological character of all water supplied for drinking purposes and if necessary, devise means for keeping it up to the standard. In many cases this means the installation of filtration and chlorination plants. The railroad

is also vitally interested in the health of its employes and the laboratory is frequently asked to check water supplies where they may be suspected of producing illness among the workers. The chemical engineer is called upon to locate and develop new water supplies on new lines that are being constructed or on old lines where increased supply is necessary or changed conditions make new supplies desirable.

Importance of Lubricants

The average passenger on a railroad train little realizes how much it costs to make the train run smoothly. The lubrication of locomotives and cars costs thousands of dollars every year and a great saving can be effected by the use of proper lubricants. The chemist is intimately concerned with this problem and is not only constantly testing the oils used for various purposes but is studying the problem from both a physical and chemical standpoint in order to improve this class of materials. The size of locomotives has increased in recent years and the steam temperatures have been raised to such a point by means of superheating that the proper lubrication of cylinders has become a difficult problem. Oils that will stand the temperature of the modern locomotive cylinder without breaking down are comparatively rare. It is therefore a matter of careful selection both by the oil company and the railroad, that results in successful locomotive operation. Greases of special composition have had to be developed to lubricate properly driving axles and other heavy parts. The subject of lubrication has therefore become a joint study between the mechanical engineer, the lubrication engineer, and the chemist.

Courtesy, Union Pacific System.

Water Softener and Storage Tank, Union Pacific System, Los Angeles, California. Capacity 30,000 Gallons Per Hour.

Fuel

Fuel, which is the most costly single item on the railroad, presents a chemical problem of some proportions. The railways of the country spend annually five hundred million to six hundred million dollars for fuel. It is therefore evident that if, by careful selection of this fuel, one per cent can be saved in heat units, the work has paid well. The fuel engineer is constantly studying the best methods of handling and burning fuel and constantly turns to the chemist for information on the composition of the fuels used. Fuels for special purposes, such as smithing coal and foundry coke, must be subjected to chemical test in order that the material shall have a low sulfur content and thus avoid injury to the materials worked.

Large amounts of nonferrous metals such as brass, bronze, and babbitt are used by the railroads as bearing metals. These must be under very careful chemical control as well as rigid physical inspection. Small amounts of certain impurities have a detrimental effect upon the life and service of these materials. When the parts made from these metals are worn out or broken, they are reclaimed by remelting, and after chemical analysis are brought up to specification and used again.

Cement is a material of construction which is constantly under the control of the chemical laboratory. The manufacture of cement is a highly standardized process but sometimes material may be shipped that does not fully conform to standard specifications. Other conditions such as deterioration in storage may affect the cement after it has left the mill. The railway laboratory makes physical and chemical tests on each car of cement purchased as well as on cement

that may have been long in storage, before being used. This procedure is necessary to guard against the failure of bridges or buildings in which it may be used.

Chemistry in Railroad Safety

Chemicals are made use of in practically all of the signalling processes on the railroad. That these signals must always be correct as a matter of safety, can be easily understood. A special oil is used in semaphore lamps, another in trainmen's lanterns. Fusees, as the colored flares are called which are put out for the protection of trains, must be of very definite chemical composition and the purity of these chemical mixtures, which produce either a red or yellow flame, is of the greatest importance for the protection of the public. Torpedoes, which are put on the rails to warn engineers of danger, are made of chemical compounds which must be correct at all times. Even the electrical equipment used in block signal operation is subject to careful chemical control.

All steel rails purchased are subjected to physical and chemical tests before being accepted. In addition to this, each rail that fails in service is examined to determine, if possible, the cause of the break and a chemical analysis is made. The facts thus found are incorporated in an annual report and from this, information is obtained which indicates which type of rails may be expected to give long life.

Under the general heading of failed material is included a great variety of broken parts of locomotives and cars which are sent to the laboratory to determine the cause of the failure. Frequently chemical analysis points out the defect. A broken tire on a locomotive driver was found to contain carbon in excess of the

specification limits. This made the tire too hard and brittle for the service for which it was intended. Examination was at once made of other tires bearing the same heat number, which had not yet been applied, and these were also found high in carbon and reported as unsafe for use. They were returned to the manufacturer for replacement, thus avoiding the possible loss of life and property which might have occurred had they been used.

The chemical department is often called upon by the claim department or the legal department to assist in cases where material is involved which requires chemical examination. The variety of these materials is illustrated by examining a single file which covers cases involving mustard, flour, cottolene, cottonseed oil, grape juice, coconut oil, flavoring sirup, metal grill work, sugar, wheat, rubber tires, sugar beet seed, burlap bagging, plaster, and others. All these offered problems for the chemist to solve.

Timber preservation is distinctly a chemical problem and one to which the railways have given much attention. By proper treatment with creosote oil, zinc chloride, or a mixture of zinc chloride with crude oil, the life of ties is greatly increased. Creosoting has been a very satisfactory process, but its high cost has resulted in studies being made to bring out less expensive processes. The work of the chemical engineer in this line is likely to result in new and improved methods for this treatment, with great saving.

The destruction of weeds along the right of way has become a chemical process. Many railroads are spraying the vegetation early in the season with solutions of sodium arsenite which kills the plants and keeps the weeds from obstructing the right of way. The increasing cost of labor in the old method of destroy-

ing weeds by hand has made this chemical process a profitable one.

Most railroads maintain an industrial department, whose function it is to induce industries to locate at points on the line where the natural resources provide an attractive field for their operation. These resources frequently involve natural chemical products such as ores, clay, coal, oil, or other substances of a mineral nature. The chemist is called upon to pass upon their value before proceeding with development work.

The reader's attention has been called to enough items to enable him to form a fair idea of the chemical side of this great industry. It must be remembered, however, that hundreds of items not mentioned here are brought before the chemical department of a railroad. It is, however, evident that there is a sufficient variety of chemical work on the railroad to avoid monotony and at the same time demand the exercise of the best chemical training and energy that can be brought to the work.

CHAPTER XVIII

RAYON—MAN-MADE SILK

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The International Exhibition held in Paris in 1889 brought a great surprise to the textile world by the introduction of a new synthetic fiber, called by the inventor, artificial silk. No one thought at the time that this new textile fiber, created by close coöperation of chemical and textile knowledge, would be the foundation of one of the most important industrial developments of the twentieth century. Within one generation the new product took its place in the industry as an independent textile fiber with applications in all lines of the textile trade. It represents today the art and refinement in textiles and is influencing our life, giving an attractive and beautiful frame to the picture of modern culture. Still further, it satisfies through its harmony of colors our present artistic desire for color, light, and luster.

The advance in art education and artistic taste called for radical changes in the development of textiles. By the study of art in schools and encouraged by many publications, art museums, and organizations like "The Art and Industries Foundation," the educated part of the population, especially the women, having the

greater artistic taste, created a demand in recent years for more lively and artistic combinations of colors and designs of texture. The post-war period further stimulated the desire for light and color, and, supported by the high average buying power which helps any industrial development, it resulted in a renaissance of the textile industry. Simultaneously, the knowledge of chemistry and its rapidly growing applications to industry found one of its many present-day realizations in the manufacture of artificial silk, known under the generic name of "rayon."

The invention of artificial silk was based on the observation of silk spinning in nature. Scientists observed how the silkworm feeding on mulberry leaves produces the silk fiber and they tried to reproduce this process in a chemical and mechanical way, using as raw material the principal component of the plant structure, which is cellulose, and spinning the solutions of its chemical compounds. The silkworm, changing from the caterpillar to the chrysalis stage in spinning its cocoon, ejects through two extremely fine openings located in its mouth a semiliquid, viscous substance which hardens immediately upon contact with the air. This is composed of two albuminous substances containing about 80 per cent fibroin and 20 per cent sericin, the latter being a soluble gum. In this way one cocoon produces an average of five hundred yards of very fine filament known as raw silk. Such a fiber is never uniform because it is not spun under uniform pressure when the worm moves around, as there is no mechanical exactness of movement or delivery of viscous mass from the glands.

Réaumur, the well-known French scientist, suggested

in his book, "Histoire des Insectes" (1734-1742), the imitation of natural silk by human artifice. In Italy, especially on one of the small Venetian islands, Murano, where the glass industry developed several centuries ago, melted glass was pulled with a pointed steel rod whereby the finest filaments of glass were drawn and reeled as a continuous thread. Dresses made of such glass silk appeared as an interesting novelty at the Grand Opera in Paris. Then the chemists turned their attention to the transformation of chemical compounds into artificial fibers, and in 1855 the Swiss, Andemars, patented a process of spinning an ether-alcohol solution of nitrocellulose, a chemical product made by the action of nitric acid upon cellulose. In 1882 Swan, Wyne, Swinburne, and Powell produced in England nitrocellulose threads for carbon filaments for use in incandescent lamps, but their process was not commercially successful. The realization of the idea actually started in 1884 when the French nobleman, Hilaire de Chardonnet, conceived the idea of forcing a solution of nitrocellulose in alcohol and ether, called collodion, through fine capillary openings. In the same year he patented a manufacturing process for artificial silk. He dreamed of replacing the expensive natural silk by such an artificial fiber and for this reason named it artificial silk, not suspecting that this crude substitute would within forty years revolutionize the entire textile industry.

The raw material used for the experiment was identical with the food eaten by the silkworm, namely, cellulose extracted from the mulberry leaves, but while the cocoon fiber is an organic product containing nitrogen and is a typical animal product, the artificial fiber was

free of nitrogen and in chemical composition was identical with cellulose. Artificial silk is a synthetic product of vegetable origin because its basis is cellulose and therefore, from a chemical standpoint, it is comparable with cotton, flax, and hemp, while natural silk and wool are representatives of products of animal origin.

Artificial silk is not made by spinning or twisting wood or plant fibers together as cotton or wool yarns are made. It is the product of a series of chemical reactions which use cellulose, a vegetable fiber, as raw material. Cellulose consists of carbon, hydrogen, and oxygen which are very abundant chemical elements in nature. Our ancestors used this cellulose in the form of leaves to dress themselves. Then cellulose in the form of cotton became the most important textile product. Now modern chemistry is changing the leaves into artificial silk to dress and please the present and future generations, and as always it is the woman who gives the inspiration and governs the vogue.

The principle of the manufacture of artificial silk is the transformation of the solution of cellulose compounds into fine, endless, solidified filaments by means of chemical reactions and mechanical appliances. This transformation is made on spinning machines of complicated nature which are of great importance in the manufacture of this commodity.

Early in the nineteenth century the paper machine was invented. At the end of the same century the development of the spinning machine for artificial silk helped to establish this young industrial development. From the raw material to the spinning machine the manufacture of artificial silk is a continuous chemical process which is carried out uninterruptedly day and

night. The transformation of cellulose to artificial fibers covers a period of about fifteen days.

The year 1891 witnessed the beginning of the manufacture of artificial silk on a commercial scale in Besançon, France, by the Société Anonyme pour la Fabrication de la Soie de Chardonnet. In 1890 a French chemist, Despaissis, dissolved cotton cellulose in an ammoniacal solution of copper oxide, but it was not until 1897 that Pauly in Germany was able to make use of this discovery for the production of another kind of artificial fiber called cuprammonium silk. In 1892 the English chemists, Cross, Bevan, and Beadle, discovered still another compound of cellulose called cellulose xanthate, formed by the action of carbon bisulfide on mercerized cellulose, which they named "viscose" on account of its high viscosity. This discovery gave the start to the viscose process of artificial silk manufacture, the method used today more widely than any other. About 80 per cent of the total world production of rayon at present is made from viscose and this growing industry is well established in the United States and Europe. About the same time Cross and Bevan produced another compound of cellulose by treating it with acetic acid and this discovery became the basis of the fourth kind of rayon, known as acetate silk.

It took about thirty years before the new textile fiber was perfected in a chemical and mechanical way to the present standard, resulting in a uniform thread of a perfectly equal diameter and strength and more uniform in all respects than the fiber products of nature. After the war, about 1920, the interest of users and investors in this new commodity began to increase rapidly, resulting in the production of rayon

which today is produced in greater quantity than natural silk.

Processes of Manufacturing Rayon

The four different processes are still used today, and have in common, cellulose derived from wood or cotton as the raw material, and are all manufactured by similar chemical and textile operations. The cotton cellulose used is in the form of linters obtained from the short cotton fibers adhering to the seed, and the wood pulp best adapted for the manufacture of artificial silk is that obtained from spruce by the sulfite process. The following table shows the preparation of cellulose.

PREPARATION OF RAW MATERIAL

Cotton Linters	Spruce Wood
Cleaning Seed	Barking, Cleaning and Chipping
↓	↓
Crushing and Pressing	Sulfite (Sulfur-lime, Calcium Bisulfite)
↓	↓
Raw Linters	Cooking in Digestors
↓	↓
Digesting with Caustic Soda	Washing and Screening
↓	↓
Washing	Bleaching (Lime—Chlorine)
↓	↓
Bleaching (Lime—Chlorine)	Washing
↓	↓
Washing	Paper Machines
↓	↓
Drying	Drying
↓	↓
Bleached Cotton Linters (Pressed and Cut in Sheets)	Cellulose (Cut in Sheets)

The chemically purified cellulose is used in the manufacture of the four different kinds of rayon according to the charts shown on the following page.

PROCESSES OF MANUFACTURE

I

NITROCELLULOSE
(Chardonnet Silk)

Purified Cotton
↓
Sulfuric and Nitric Acids
↓
Nitrocellulose
Dissolved in Alcohol and Ether
↓
Filaments Coagulated
Nitrocellulose Filaments
↓
Recovery of Solvents
↓
Removal of Nitro Groups
↓
Unbleached Thread
Bleaching
↓
Commercial Thread

II

CUPRAMMONIUM SILK
(Also called Glanzstoff or Pauly)

Purified Cotton or Wood Pulp
Dissolved in Ammoniacal Copper Solution
↓
Spinning Solution
↓
Coagulated by Caustic Soda or Sulfuric Acid
↓
Filaments of Cellulose
↓
Bleaching
↓
Commercial Thread

III

ACETATE SILK

Cotton or Wood Pulp Purified
↓
Acetic Anhydride, Acetic Acid, and Sulfuric Acid
↓
Dissolved in Acetone
↓
Spinning Solution
↓
Cellulose Acetate Filaments
↓
Commercial Thread

IV

VISCOSE SILK

Bleached Spruce Pulp
or
Cotton Linters
Caustic Soda
↓
Soda-Cellulose
Carbon Bisulfide
↓
Soda-Cellulose-Xanthate
Water
↓
Viscose Solution
Spinning Solution
↓
Crude Viscose Filaments
↓
Removal of Sulfur
Bleaching
↓
Commercial Thread

NITROCELLULOSE PROCESS

In the nitrocellulose process, the bleached cotton is nitrated in an operation similar to the manufacture of smokeless gunpowder. Cotton linters are immersed for a period of time at a constant temperature in a

mixture of nitric and sulfuric acids in a centrifuge. Then the excess of acids is removed, regenerated, and used again. The nitrocellulose so obtained is washed with water until all acid is removed. The nitration of cellulose is an operation which requires very careful control in regard to the chemical composition and temperature of reaction.

The nitrated cotton, consisting mostly of trinitrocellulose, is dried slightly and mixed with ether and alcohol in slowly rotating tanks until a solution of sirupy consistency called collodion is obtained. Then the solution is passed under pressure to a set of filter presses to remove the insoluble impurities and particles which have not been completely nitrated. The collodion solution is forced by pressure to so-called spinning machines where the liquid is pressed through capillary glass tubes, and the ejected semiliquid streams emerging from the orifices are collected in groups under tension on rotating cylinders or spools placed in the upper part of the spinning machine. During the formation of filaments, hot air is blown under the covers of the machines in order to evaporate the solvents used in making the collodion. As the solvents are removed the nitrocellulose, now in the form of filaments, solidifies.

The thread wound on the spools consists of several fine filaments which are then twisted on fast rotating vertical spindles on twisting machines, whereby the twisted yarn is wound on horizontal take-up bobbins. The raw yarn is then removed from the bobbins by reeling into the commercial form of skeins on reeling machines.

The yarn, consisting of nitrocellulose, is inflammable like guncotton, and a further chemical treatment is necessary to remove its explosive character by a proc-

ess of denitration whereby the nitro groups are removed and the thread is left as pure cellulose. This denitration is effected by treatment of the skeins with a warm solution of sodium hydrosulfide. Then the chemicals are removed by washing, the uniform white color of the yarn is obtained by bleaching, and after drying and examining, the skeins which are several thousand yards in length are ready to be shipped.

This process is quite expensive on account of the high cost of the chemicals used. The solvents, alcohol and ether, are partly recovered and used again for dissolving nitrocellulose.

Cuprammonium Process

A solution of cellulose in ammoniacal copper oxide is the basis of the second process established in this industry. Bleached cotton linters or wood pulp are mixed with fine copper hydrate, and the mixture is dissolved in concentrated ammonia. The resulting blue solution should always have uniform viscosity, also the same copper and cellulose content. The usual solutions contain 3 per cent copper, 7 to 8 per cent ammonia, and 7 to 8 per cent cellulose.

The next step is the filtration of the viscous solution to eliminate undissolved foreign matters, as the liquid in forming filaments is forced during the spinning process, through minute orifices and any solid particles contained in the liquid would obstruct the passage and cause the delicate fibers to break. For the same reason air bubbles are removed by vacuum. The purified solution now arrives at the spinning machines and is forced through fine holes called spinnerettes into a setting bath of sulfuric acid or caustic soda. Some manufacturers are applying both chemicals—first

caustic soda, and later, for the purpose of final setting, dilute sulfuric acid. Thereby fine filaments are produced similar to the nitrocellulose process.

After the spinning, traces of chemicals must be entirely removed from the fibers by washing with water, because they would affect the quality of the fiber during the subsequent drying. The next and last operation is the bleaching, which results in a purified white product that is very soft to the touch and possesses high luster. The yarn can be dyed in colors by the application of direct dyestuffs, the same as those used for cotton. An important factor in this method is the recovery of the copper and ammonia in a separate chemical plant.

One of the methods used today is based on the experiment of Thiele in Germany. It is the "stretch spinning process" which resulted in the production of very fine filaments of a size as fine or finer than the cocoon fiber. This improved cuprammonium process was used on a larger scale before the viscose process was developed. In recent years most of the plants in Europe which previously used this system, have changed over to the viscose method.

Acetate Process

Cellulose has the formula $C_6H_{10}O_5$, and contains three hydroxyl (OH) groups. By the treatment of cellulose with acetic acid, two or three acetyl groups are introduced into the hydroxyl groups, acetyl being a part of acetic acid, and the resulting derivative is called cellulose acetate or acetic ester of cellulose. This product is soluble only in organic solvents such as acetone or chloroform like nitrocellulose, which is soluble in alcohol-ether, but unlike the cuprammonium product.

In 1894 C. F. Cross patented the first manufacturing process for cellulose acetate. His process consisted of treating purified cotton with zinc acetate and acetyl chloride, two compounds well known in the chemical practice. In this country in 1905 Miles obtained a high-grade product by subjecting the cellulose acetate during its preparation to a special process of ripening. This method permitted the manufacturing of acetate silk and noninflammable photographic films on a commercial scale. The research work of the brothers Dreyfus in England and in this country during and since the war, resulted in the development of the acetate silk industry.

Bleached cotton linters are treated in large jacketed and enameled vats with acetic anhydride in the presence of glacial acetic acid and sulfuric acid until the mixture goes into solution. This process requires careful supervision and several chemical control tests. The resulting cellulose acetate, which is a mixture of several acetate compounds, is precipitated with water in form of white flocks, washed until it is free from acid, dried, and dissolved in acetone. The resulting clear viscous solution is filtered carefully and delivered under pressure to spinning machines where the spinning process is performed, as previously described. The vapors of the solvents are removed, condensed, and used over again in the preparation of solution.

The resulting filaments spun in groups are twisted in the usual way and placed on the market as cellulose acetate, unlike the products of the other systems in which the commercial fibers consist of pure cellulose. Acetate silk is sold in this country under the trade names of "Celanese" and "Lustron."

The expensive chemicals like acetic acid and acetone are partially recovered during the process, but never-

theless this method is expensive and has not yet found a large application in the industry. The resulting yarn does not absorb moisture as readily as the other kinds of artificial silk, and therefore it has less affinity for dyes. This property has so far prohibited its use on a large scale in the textile industry.

Viscose Process

Of all the known methods of artificial silk manufacture, the viscose process has found the greatest application and is used on a large scale in this country. As said before, about 80 per cent of the total present world production of rayon is made according to this method. As raw material, bleached spruce pulp, cotton linters, or a mixture of the two is used. The silk from pulp has a mild, not opalescent luster and dyes more uniformly than that derived from cotton. The pulp, cut in rectangular sheets, is soaked in an 18 per cent caustic soda solution, this treatment causing the fibers to swell and form a compound known as soda-cellulose. The excess of caustic soda is removed in hydraulic presses and after reclaiming is used over again.

Thereafter the sheets of soda-cellulose are shredded to fine crumbs and conveyed to small containers where the soda-cellulose remains at a constant temperature for a period of time undergoing an aging process. The uniform and properly aged soda-cellulose is now transferred to a double-jacketed, air-tight, rotating container where it is treated with carbon bisulfide. This treatment results in the formation of yellow-orange crumbs, a product called cellulose xanthate. The reaction is very delicate and must be controlled carefully to obtain a uniform final product. The purpose of this chemical reaction is to transform the insoluble cellulose into a

Courtesy, The Industrial Fibre Co.

Hydraulic Presses for the Mercerization of Cellulose.

water-soluble compound, and the resulting solution after preparation in well-insulated, double-jacketed mixers at a low and uniform temperature is called "viscose." The orange-colored, viscous liquid is pumped to the ripening department, where it remains again at a low uniform temperature for a period of time before it is transferred under pressure to the spinning machines. It is also filtered carefully and freed of air bubbles by vacuum before it is converted into filaments.

The viscose is now pumped through mechanical regulators which are placed on the spinning machines, each regulator pumping a constant amount of viscose to the outlets fitted with platinum nozzles. The solution forced through the minute holes of the nozzles is divided into very fine streams which, passing through the precipitating bath of sulfuric acid and other chemicals, are immediately coagulated and the streams of viscose solution are converted into fine filaments of regenerated cellulose. The size of the spun thread is determined by the amount of solution of known cellulose content projected through the nozzle in unit time and by the rate of speed at which the thread is collected. As in the previously described methods, the collected filaments are converted into skeins of twisted yarn.

The viscose process requires the continuous attention of the chemist during several complicated stages, for unstable compounds are being formed. The working formulas must be established entirely independent of climatic conditions, and the slightest irregularities in the chemical process must be avoided, as they would influence the product and might mean the difference between success and failure.

During the spinning of viscose, different by-products are formed containing sulfur derived from the carbon bisulfide used. These impurities are removed from the

skeins by treatment with sodium sulfide solution and bleaching with chlorine. These operations are also very delicate because they may cause destruction of the yarn. After bleaching, antichlor is applied to remove the traces of chlorine and the skeins are then washed until all chemicals are eliminated, the excess water is removed by a centrifuge, and the skeins are dried. From the drier the skeins enter the inspection department where each skein is examined and graded for quality, great care being taken to see that the silk absorbs a uniform amount of moisture from the atmosphere. Finally the skeins are wrapped, and bundled under pressure in ten-pound packages ready for shipment.

The size of rayon yarn is defined by the metric denier standard, the same as employed in measuring the size of raw silk. The finer the silk, the smaller is the denier. Two standard sizes, namely 150 and 300 denier, are the most frequently used in the textile industry. Ten thousand yards of yarn weighing 150 grams are 150 denier; similarly, ten thousand yards of yarn weighing 300 grams are 300 denier. Accordingly, one pound of 150 denier contains 30,000 yards and one pound of 300 denier 15,000 yards. The corresponding sizes of cotton are Nos. 30 and 15, respectively, No. 1 cotton yarn having 840 yards to a pound.

Properties of Rayon

One ton of purified sulfite pulp produces in the manufacturing way about 1500 pounds of silk, equal to forty-five million yards of standard yarn. One spinner produces every day in eight hours three million yards of the same standard. The price of wood pulp is about five cents a pound and that of a good grade of rayon, two dollars a pound. This difference in price is a good

Courtesy, The Industrial Fibre Co.

Twisting and Reeling Rayon.

illustration of the value and earning power of research, which, based on the ingenuity of chemists in applying intricate methods, is able to increase many times the value of the raw material. It also shows in dollars and cents the financial power and value of chemistry in industrial applications, the chemist's work in this industry being a transformation of one kind of cellulose into another. Of great technical importance in the rayon industry is the mechanical equipment, the organization of production, and the continuous chemical control of complicated processes. The coördination between the mechanical and chemical operations requires the highest precision in each stage of the continuous process, whereby the consecutive stages must be synchronized and correlated under detailed attentive control of management.

Rayon manufacture is today a well-established industry, based on skilled labor and technical ingenuity combined with common and most abundant raw materials and chemicals obtainable all over the industrial world.

Artificial silk is a soft, pliable, multi-filament textile fiber which owes its large application in all textile commodities to its uniformity, fine luster, and high dyeing quality. Like all other kinds of textile fibers, rayon must resist wear and tear, and the desire of our present industry is still further to increase the strength of artificial silk. Fabrics made of rayon or of mixed fibers containing rayon must be handled carefully, like any kind of delicate fabric. Rayon partly loses its strength while wet, but regains its previous strength after drying. If handled carefully, rayon resists all the usual treatments with chemicals, also higher temperatures; for instance, boiling water can be applied without detrimental results. Generally, rayon garments should be

washed by hand at a temperature of 150° F., with a good grade of neutral soap.

When the rayon industry began to develop and only nitrocellulose silk was in use, a general opinion was formed that the product was inflammable. This prejudice has disappeared and today rayon is regarded as no more inflammable than cotton or other kinds of textile fibers.

The work of a productive chemist is not only to make the invention but to manufacture the product and to adapt its qualities to any kind of application. The weaving industry requires a fiber which has a high covering power, imparting full body to the fabric. This property has been greatly improved in the manufacture of rayon thread by the application of special chemical reactions during the precipitation of the fiber, whereby round or flat filaments are produced by altering the composition of the setting bath. Also, waterproofing of artificial silk has been greatly improved. When treated with water the fiber absorbs a large amount of liquid, increasing in volume by 40 per cent, but when dried it contracts and regains its former volume. This ability to gain and lose water is due to the capillary structure of the fiber and the large surface of the filaments. Its physical structure can be changed by chemical reactions and there are many processes known for the waterproofing of artificial silk, one called Sthenose being based on the treatment of the yarn with formaldehyde and lactic acid.

On the other hand, the power of absorption of moisture is an advantage of rayon when used for underwear, because it absorbs the perspiration from the body and permits the evaporation of the excess moisture, thus keeping the skin dry and comfortable. This hygienic property has but recently been recognized to

Figure 5

A—Natural Silk
B—Artificial Silk
C—Cotton
D—Wool
E—Wood Pulp

be a great advantage, and artificial silk combined with cotton or real silk is used more and more as an ideal yarn for shirts and underwear. It has still another advantage in this respect, because natural silk rots from perspiration and turns yellow, while artificial silk remains white. Real silk is generally weighted with metallic salts, in some instances, as in black fabrics up to 300 per cent of the original weight of the yarn, and this content of foreign matters makes silk brittle and is not conducive to good health. Artificial silk, however, is never weighted; it is a pure cellulose product and, therefore, has no injurious effect on the skin. The gloss and brilliancy of artificial silk surpass that of natural silk and all other fibers, because the individual filaments are flatter and present a greater light-reflecting surface than the cylindrical natural silk fibers which reflect a relatively smaller amount of light.

The different kinds of rayon have not the same luster, nitro silk being shiny, copper silk glassy, and viscose silvery, more like natural silk. Also the feel of viscose silk is similar to natural, but slightly colder and harsher to the touch. Any degree of softness of rayon can be produced during the manufacture, the softness being the result of the number of single filaments drawn from the cellulose solution. The rayon filaments can be spun as fine as cocoon fibers.

Artificial silk may be identified by its chemical and physical properties, the simplest test being the combustion test. It burns like cotton with an odorless flame and leaves no residue but a small amount of ash, while natural silk and other animal fibers smoke without burning, giving off a disagreeable odor like burnt horn, and leave a charred residue. Natural silk and wool dissolve in a concentrated solution of caustic soda,

while artificial silk swells slightly but does not go into solution.

Applications of Rayon

In all branches of the textile industry, rayon is used independently of other textile fibers or in a supplementary way. With cotton it is used to a large extent for underwear, hosiery, ribbons, all kinds of pile fabrics, shoe coverings, cloths, umbrellas, and for wire insulation. It finds a growing application for bedspreads, draperies, trimmings, elastic webbing, satin, laces, embroidery, and being more resistant to friction than natural silk, it is valuable for hat and coat linings. It is replacing cotton in many fields, because the supply of long staple cotton has been greatly reduced and its price is gradually approached by artificial silk which in addition has the advantage of being produced in endless lengths.

Growers of cotton will not be forced out of business by the growth of the artificial silk industry, but it may reduce the production of cotton and stabilize prices and establish reasonable profits for the cotton industry. Part of the cotton production, namely the short linters, will find its place in the rayon industry as raw material. Many authorities claim that cotton in the future will be replaced entirely by artificial silk. However, this expectation has no foundation, considering the present stage of development of this young industry. Should this ever take place, it will not be in a revolutionary way but by means of slow adaptation and chemical evolution during the generations to come. It is more probable that the agricultural conditions of the country will be adjusted. The supply of wood for pulp in this country may be exhausted unless a radical reforesta-

tion policy is established. It would be also beneficial to cotton growing if the reforestation of the cotton belt were encouraged, thus better protecting the parts of land used for cotton. Another solution of the competition between cotton and rayon would be to find better methods of mercerization to increase the value of cotton, and this would again be the function of the chemist. To the great task of the chemist within this industry may be added his worries about cotton and rayon, which are like those intimated in the sign on a livery stable, "Horses clipped and rubber tires put on."

In combination with natural silk, rayon is used largely for hosiery, ribbons, silk fabrics, and brocades. It is used for crepes, mousselines, fur imitations, plush, and velvet. It has further use for the skeletons of gas mantles, toys, artificial hair, and for millinery purposes either alone or in combination with metallic cloth. Artificial silk waste is corded, combed and spun with wool or used alone for fringes, tassels, button coverings, and felt. Artificial horsehair and artificial straw, known on the market as "Visca" and used for millinery purposes, are also made from viscose. The product is obtained during the spinning process by pressing the solution through nozzles of a different size and shape than those used for rayon. Rayon is also used in connection with rubberized cloth for surgical dressings, and being a poor conductor of electricity, it is used for insulating purposes on electric wires and magnetos.

A generation ago when in England the first attempt was made to manufacture artificial silk, people having a prejudice against the new result of chemical development laughed, claiming that "they try to make silk stockings out of cabbage." Today, this prejudice has been overcome and there is not one branch of the tex-

tile industry which would hesitate to use rayon or deny the good results obtained.

Dyeing of Rayon

One of the most striking advantages of rayon, especially of the viscose product, is the dyeing quality. It takes the substantive and basic colors, the latter with or without mordant, very uniformly, resulting in brilliant colors of the yarn. If fabrics made of wool or natural silk mixed with rayon are dipped in a dye-bath containing two different dyes, two or three color effects are obtained simultaneously, a process known as cross dyeing which is applied to brocades and other fabrics. Similar are the results of alternate weaving together of viscose and acetate silk which have a different affinity for the same color in the dye-bath. In the printing of mixed or rayon fabrics, it is possible to produce very elaborate color designs with striking effects at a much lower cost than would be the case if the fabrics were produced by weaving the different colors on Jacquard machines. On the printing machines as many as eighteen different colors can be produced simultaneously on one fabric. This produces a rich material striking in depth of color and beauty of design, and such fabrics are used for expensive gowns and neckties. The gift of an artistically woven and dyed or printed dress made of rayon is appreciated by many wives and daughters, although they may still prefer jewels instead.

World and Domestic Production

According to the records of the Textile Division of the Department of Commerce at Washington, D. C., the domestic production of artificial silk increased from

one and one-half million pounds in 1913 to thirty-nine million in 1924, the latter output representing a value of about eighty million dollars. The world production in 1913 was about twenty million pounds and in 1924 the one hundred million mark was passed, of which almost 40 per cent was produced in the United States. The production and consumption of rayon are today far in excess of that of natural silk and according to some authorities, are nearly double. The domestic production is growing rapidly and about one hundred million dollars of capital are invested in this industry. The superior quality of rayon made in this country and the efficiency of the manufacturing methods enable us to compete with countries where labor is cheaper and make us independent of imports. In 1923 seven million dollars' worth of rayon was imported by this country from Europe and in the following year the imports dropped to two million dollars. The imports supply our domestic market with lower and cheaper grades than those produced here and this reason, added to the rapid growth in the production of artificial silk in this country, explains the gradual diminishing of imports from foreign countries.

The United States is today the largest producer as well as consumer of artificial silk, because the industry is built on large-scale production and the success of the operations depends upon large financial reserves. The process is intricate and requires the handling of large amounts of material for a long continuous period of time on complicated and expensive machinery.

Opportunities for Chemical Research

Is artificial silk an ideal fiber? There are several problems to be solved before this question can be an-

swered favorably. The present process of manufacture requires a long run and the study of the technical chemist may result in a shorter process. He must study the different reactions of aging, with a view toward shortening the time. Uniformity of the aging process must be established and controlled by means of simple testing methods. The by-products resulting from the reactions applied in the manufacture have also commercial value, and the study of methods for their complete recovery is another important field for chemical research. Other by-products like hydrogen sulfide, generated during the transformation of viscose solution to cellulose thread, must be eliminated as they affect unfavorably the manufacturing process and involve complicated systems of ventilation. The chemical and physical control of testing methods of this young industry is not yet standardized. The knowledge of organic chemistry and analytical ability are necessary to study and perform the complicated research supported by continuous observation of all the reactions involved. Also a knowledge of textile operations is necessary because the consumer having difficulties in the handling of artificial silk will always refer complaints about the yarn to the manufacturer. The chemist must have artistic taste to judge the color, touch, and luster of the yarn itself and the fabrics made from it.

Rayon loses part of its strength when in a wet state and the problem of its water resistance gives the greatest opportunity to the chemist. Rayon produced in such quality that its strength while wet will be almost or entirely equal to the strength of the dry product would be a dominant factor in the entire textile industry. What becomes of the waste of rayon dresses? Con-

sisting of pure cellulose, this could be utilized as an ideal raw material in this growing industry.

The preservation of natural resources is also the task of the chemist who may be able to synthesize the wood, the raw material for rayon. The structure of cellulose is not yet defined, therefore analytical methods for testing raw material are not perfected. The chemical behavior of cellulose in the processes depends on the climatic conditions under which the plant cellulose grows, the result being that the cellulose in physical structure and chemical composition is not homogeneous and is often beyond technical control during the manufacture of artificial silk. The textile industry based for centuries on mechanical traditions at first mistrusted the chemist. Today, evolution of the textile industry through the introduction of the synthetic fiber is on the way to be accomplished satisfactorily, resulting in refinement of blended fabrics and harmonious lively colors.

Chemical research on such problems is the foundation of the industry. It is comparable with the financial budgeting of any commercial organization. Chemistry as a science is the organized knowledge of matter and energy, and if applied in a productive way to the industry, it spells success.

Reading References

Becker, Franz. Die Kunstseide. Wilhelm Knapp, Halle, 1912.

Cross, C. F., and Bevan, E. J. Cellulose. Longmans, Green & Co., London, New York, 1918.

Cross, C. F., and Bevan, E. J. Researches on Cellulose. Longmans, Green & Co., London, New York, 1913.

Foltzer, Joseph. Artificial Silk and Its Manufacture. Sir Isaac Pitman & Sons, Ltd., London, 1921.

Margosches. Die Viskose. 1906.

Suevern, C. Die Kuenstliche Seide. 1920.

Tariff Information Surveys. Artificial Silk. U. S. Government Printing Office, 1925.

Wheeler, Edward. The Manufacture of Artificial Silk in Relation to Colloid Chemistry. Fifth Report on Colloid Chemistry, 1923. British Association for the Advancement of Science.

Worden, E. C. Nitrocellulose Industry. D. Van Nostrand Co., New York, 1911.

CHAPTER XIX

CHEMISTRY IN REFRIGERATION

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The simplest refrigeration plant is the ordinary household refrigerator or icebox. Here a piece of ice is placed in such a position in the icebox that the air surrounding the ice may cool and fall away, to be replaced by warmer air for the same reason in reversed sense that air rises from a heated object. By means of this air circulation over the cake of ice, it is generally possible to obtain a sufficiently low temperature for food preservation and similar purposes.

Ice distributed by the familiar ice wagon is common enough in the United States, but elsewhere in the world ice is scarce or nonexistent and refrigeration for manifold purposes must be accomplished in other ways. Indeed, one of the earliest devices employed depended upon a fundamental principle illustrated often for classes in physics. In this experiment a quantity of water is placed in a Dewar or thermos bulb and connection made with a vacuum pump. Upon working the pump the air is first withdrawn. Finally the water boils or evaporates and then begins to congeal to form ice. Those who remember the experiment may also retain the explanation of this simple but fundamental experiment. The formation of the ice depends upon

the fact that whenever a substance such as water changes its state from liquid to gas or from liquid to solid and vice versa, energy is given off or taken in, depending upon the direction of the change.

Now the natural world exhibits matter to us generally in three states, a solid state, a liquid state, and a gaseous state. The change from any one state to another invariably involves a change in energy, and in general the largest change in energy takes place when a gas is condensed to a liquid state, or conversely a liquid to a gaseous or vapor state. We owe the discovery of this phenomenon, called latent heat of phase transformation, to Dr. Joseph Black (1728-1799), the Scotch chemist who included his ideas about latent heat in his chemical lectures at the University of Glasgow.

Early Experiments with Artificial Ice

Joseph Black was the pupil and successor of Dr. William Cullen, lecturer in chemistry in Edinburgh, who in 1755 succeeded in forming ice artificially by the method already referred to of evaporating water by means of an exhaust pump. In this experiment water is rapidly changed from the liquid state to the gaseous or vapor state. The transfer of state from liquid to gaseous requires heat which is supplied, as Black showed, at the expense of the heat stored in the water itself, its container, and also the surrounding air. When this stored heat is used up, the water is sufficiently cooled to begin to freeze in order to supply the further energy removed in the transfer from liquid to vapor.

Over sixty years later Sir John Leslie, using this same process and aiding the pump by absorbing the

vapor of water in sulfuric acid, succeeded in making from one to one and one-half pounds of ice in one operation. Many attempts by others to improve Dr. Cullen's original process followed, with the result that a machine was finally designed by Fleuss capable of giving about three pounds of ice per pound of sulfuric acid.

Clearly then the process of abstraction of heat or refrigeration depends on the absorption of energy attending the evaporation of a liquid, or in the more precise general language of science, on a change of phase. However, during the one hundred years following Black's discovery of latent heat and Cullen's application, with successive attempts to perfect the latter's process, a multitude of scientific principles were discovered and an increasing acquaintance with the properties of matter was the fruit of the painstaking study of the founders of modern science.

Thus Joseph Priestley (1774) succeeded in obtaining ammonia from its bases and called it according to the nomenclature of his day "alkaline air." He noted its extreme solubility in water, a fact later to be put to extensive use in the water-absorption type of refrigerating process. Robert Boyle and Joseph Louis Gay-Lussac discovered the properties of gases which, with the accumulated knowledge of the nature and properties of heat at length enabled refrigeration to be obtained by compressing vapors to the point of liquefaction at ordinary temperatures or even subsequently by expanding compressed air.

It was Michael Faraday who showed (1832) the relation of pressure to the liquefaction of gases. These studies, extended and quantitatively pursued by the Irish chemist and physicist, Thomas Andrews (1813-1855), revealed with much completeness the general properties of substances. In particular the complete

relation between the liquid state and the vapor state as dependent on the temperature and the pressure was disclosed for the first time. It became clear from Andrews' investigations why the attempts to liquefy such gases as nitrogen, oxygen, or hydrogen had failed, confirming the thought of Faraday that there existed an upper limit of temperature above which it is impossible for a gas to be condensed to a liquid regardless of the magnitude of the pressure. The latter temperature, called the critical temperature, is a most important constant for a substance and has been measured for over two hundred pure chemical compounds.

The development of the theory which was to supply the basis of design and performance of refrigerating machinery had not lagged in the hundred-year period following the discovery of the property of latent heat. Count Rumford, of American birth, had made fundamental experiments showing that heat was a form of energy and not a substance. Sadi Carnot (1824) gave the equation which related the work obtainable by a heat engine with the quantities of heat available at different temperatures. Mayer (1814-1879), Joule (1818-1869), William Thomson (1824-1907), Clausius (1822-1888), von Helmholtz (1821-1894), and others perfected the theoretical structure which today comprises the general subject of thermodynamics and without which the intelligent design of refrigerating plants, steam plants, or the like would be impossible. Indeed, modern theoretical chemistry rests broadly and solidly upon this same theoretical structure of thermodynamics or the theory of heat.

Refrigeration Machines

The attempts to construct refrigeration machines, employing the evaporation of a liquid as a means of

abstracting heat, were numerous before the theoretical foundation necessary for intelligent design was provided. Also the principle underlying the operation of a steam engine where a drop in the temperature of the steam takes place when it is allowed to expand against the engine's piston, had been applied to the refrigeration problem. Here compressed air was allowed to replace the steam and the cold exhaust air used to freeze water, cool brine, or refrigerate directly.

The method wherein the latent heat of an evaporating liquid is the means by which heat is abstracted may be applied in essentially two ways. One method is known as the compression system, the other as the absorption system. In addition to these two types, a machine which uses a compressed gas, usually air, and permits it to expand in an engine with attendant cooling constitutes a class by itself and is often referred to as a dense air refrigerating machine. Thus there are three kinds of refrigerating machines, the compression, the absorption, and the dense gas machine; the first two kinds depending, as already stated, on the absorption of heat by the transformation of a liquid to a gas, and the third depending on the cooling of a gas when it is allowed to do work as in the steam engine.

Compression Machines

As examples of early attempts to build compression machines reference may be made to an American engineer, Jacob Perkins, living in London, who designed and patented an early compression machine employing ether in 1834. The first semipractical, though inefficient, machine was not built, however, until 1861 and was used to cool oil for the extraction of paraffin. Thus in the refrigeration art there happened essentially what

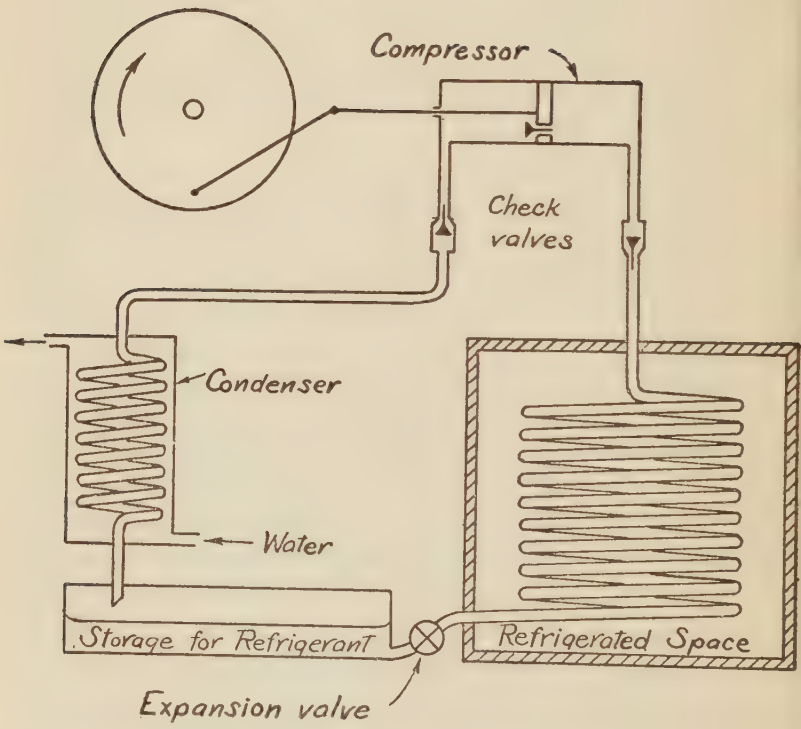
is repeated in the history of all arts: a long pioneer period of "cut and try" attempts to build refrigeration machinery before the precise scientific basis for design was recognized. There appeared, however, in 1870, a very important paper entitled "The Removal of Heat by Mechanical Means" by a Zurich engineer named Carl Linde. Here for the first time the basic thermodynamic theory was applied to the mechanical refrigeration problem. The Brewers' Congress in Zurich in 1873 pledged the financial support necessary to build the first machines.

Carl Linde's first machine employing sulfur dioxide was completed in 1874 and tests made subsequently confirmed the soundness of the design by showing efficiencies far in excess of anything previously obtained. Various refrigerating fluids were tried, but ammonia was used after 1877. The elements of design were now understood and there followed everywhere an improvement in design and an extension of the use of mechanical refrigeration by the compression system.

The compression machine in its simplest conception consists of a compressor, a condenser, an expansion valve, a reservoir tank or receiver, and an evaporator.

The compressor (Fig. 1) on the stroke from right to left draws vapor into the cylinder from the evaporator coils where it boils or is evaporated, thereby abstracting heat from the surroundings in which the coils are placed. The next stroke from right to left compresses this gas and sends it to the condenser where it is condensed to the liquid state. Here the latent heat is given up to the cooling water and the adjustment of the expansion valve finally permits the liquid to pass in the desired amount to the evaporator coils, where it is reevaporated by the motion from right to left of the piston of the compressor. In the diagram a check

Fig. 1



Compression Machine

valve is placed in the suction side of the compression line and also in the compression side. A valve is also represented in the piston itself, opening on the stroke from left to right. The suction check valve, on motion of the piston from left to right, retains the vapor drawn into the cylinder during the right to left stroke, compelling it to pass through the piston valve to the left side of the piston. The check valve in the compression line meanwhile prevents the passage of vapor or evaporation of the liquid from the receiver through the condenser. The stroke from right to left closes the piston check valve and forces the compressed vapor through the compressor check valve, at the same time again drawing evaporated vapor from the evaporation coils through the suction check valve. These check valves open only in the direction of the arrow.

The foregoing outline in principle represents the action of the compression system. It will be noted that the function of the compressor is essentially to raise the evaporated gas from the low pressure under which it exists at the low temperature in the evaporator coils to the pressure where it may be condensed or converted to the liquid state at the temperature of the cooling water.

Absorption Machines

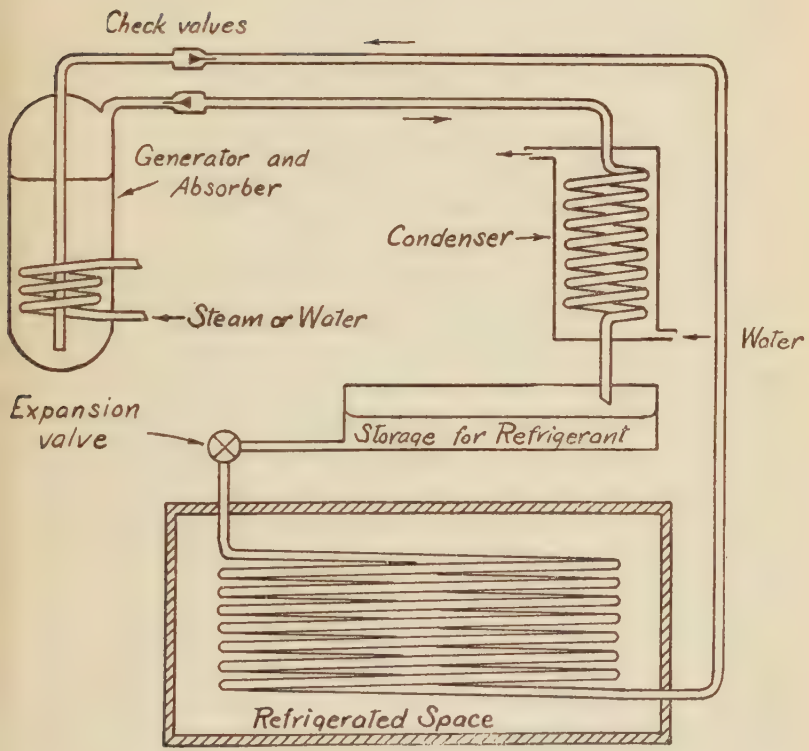
The absorption system hitherto has existed in the form of a water-ammonia absorption machine. It is possible to conceive of a system, however, capable of supplying refrigeration on this general principle wherever a gas is absorbable by a solid or a liquid. With the water-ammonia absorption machine very large amounts of ammonia are of course absorbable. Thus at the freezing point of water a pound of ammonia will be absorbed in a pound of water under a pressure

of ammonia equal to the atmosphere. On subsequent heating of such a solution, the pressure of the ammonia increases very rapidly as compared to the water and if the heating is continued to a sufficiently high temperature, a pressure will be attained at which the ammonia, together with a small proportion of water, may be condensed to a liquid at the temperature of ordinary tap water. Cooling the vessel containing the water from which the ammonia has been driven by heating allows the condensed ammonia to be re-absorbed, thereby abstracting heat from the point where the liquid ammonia is permitted to evaporate.

In Figure 2, for example, there is represented a vessel or boiler holding a strong solution of ammonia and provided with a coil into which steam may be turned or water admitted, depending upon whether the generator is to be heated or cooled. Upon heating the ammonia, the pressure rises and the gas passes through the check valve to the condenser where it is condensed to a liquid and flows into the receiver, from whence it can be allowed to flow (through an expansion valve) as required into the evaporator coils. At the completion of the heating part of the cycle, the generator is cooled, becoming an absorber and sucking the ammonia through the second check valve. The evaporation of the ammonia in the evaporator coils abstracts heat in precisely the same manner as in the case of the compressor machine represented in Figure 1.

The water-absorption machine, while simple in principle, is complicated by the fact that the water is somewhat volatile and passes over in certain proportion along with the ammonia. In practise the water is separated in what is called the rectifier and analyzer. The action here is essentially that of fractionally separating

Fig. 2



Absorption Machine

two volatile components as illustrated in separating alcohol and water by distillation.

It is conceivable that the water may be replaced by a salt capable of absorbing ammonia and a number of salts such as ammonium nitrate and ammonium sulfocyanate are known to absorb considerable quantities of ammonia. In this case an advantageous simplification results because of the possibility of employing anhydrous ammonia and thus avoiding the separation of a second volatile component such as water in the water-ammonia absorption machine. The use of ammonium nitrate has actually been tried by Seay and patents have been granted covering the use of the material.

The water-ammonia machine was early exploited by Carré in France and the machines were imported into the United States as early as 1863. Indeed, in the United States the water-ammonia system has been very much perfected in large sizes. Indications, moreover, are not wanting that the chemists will develop absorbents and adsorbents which will introduce this general type of machine into very widespread use in the rapidly developing field of small refrigerating units and perhaps even for several ton capacity.

Charcoal, which adsorbs fairly large quantities of ammonia, might also be used, but here the efficiency would be very small owing to the considerable heat needed to disengage the ammonia when adsorbed on charcoal. Silica "gel," which adsorbs (condenses on the surface of its pores) large quantities of water, is reported to be under development as a refrigerating device, and indeed it is clear that any substance may be employed in principle which is capable of uniting with large quantities of a gas. Thus to consider an unusual example, calcium carbonate could be employed

in a generator where, upon heating to a high temperature, a pressure of carbon dioxide would develop sufficient for liquefaction of the carbon dioxide at ordinary temperatures. Cooling the calcium oxide resulting after the disengagement of the carbon dioxide would cause the carbon dioxide to be evaporated in the evaporator coils and adsorbed by the calcium oxide with attendant refrigeration. The amount of energy required, however, to heat the calcium carbonate and drive off the carbonic acid would be enormous as compared with the refrigerating effect and make this particular process absurd from an economic point of view.

Compared to the compression system of refrigeration it is clear that the absorption system must be less economical from the point of view of the cost of the energy required for driving the compressor or heating the generator of the absorption system. In the latter heat must be supplied to drive off the gas from the absorbent, and for the water-ammonia solution the heat required to disengage the ammonia from solution is larger than the latent heat of evaporation which supplies the refrigerating effect. Comparing then large systems of the same refrigerating capacity, the absorption system would consume several times more energy than the compression system.

In small refrigerating units, however, such as are coming into use for household refrigerator boxes, opportunity is offered for the absorption or adsorption system, because efficiencies are not a matter of much concern where the absolute amount of refrigeration required is small. The simplification of apparatus and freedom from wearing parts would seem to be features recommending the absorption type of small refrigerating unit. There is in fact on the market at the present time a water-ammonia household unit and a solid-

absorbent-ammonia unit in addition to the numerous compression units. It is of significant interest that to date approximately $60,000,000 has been expended in the small unit development field. This development has, moreover, been principally in the field of household installations.

Dense Air Machines

The third manner of obtaining refrigeration whereby the operation of the steam engine is, so to speak, reversed, is exemplified by the so-called dense air machine. The development of this machine is largely due to an American, Dr. John Gorrie, a physician, who was granted patent No. 8080, August 22, 1850. The endeavor is of great interest, not alone from the point of view of refrigeration, but because of the altruistic motives of Dr. Gorrie, whose object was to allay suffering and aid in the treatment of fever cases by providing an adequate supply of ice.

The machine consists in principle of two engines, one of which compresses the air, the second being driven by the air compressed by the first. The power obtained from the second system may, of course, be used to assist in driving the air-compressing part of the apparatus. The operation depends upon the fact that whenever a gas is compressed it warms and in the compression cylinder of the dense air machine water cooling is used to remove the heat of compression. The air, therefore, enters the expanding engine at cooling-water temperature and after moving the piston passes out at low pressure and temperature. The expansion is entirely analogous to the action of a steam engine where, for example, steam at 300° F. and 75 pounds

pressure enters the cylinder of a steam engine and issues at 212° F. and 15 pounds pressure.

Dr. Gorrie's machine was followed by others and in this country Leicester Allen designed machines which were much used on shipboard and by the U. S. Navy. The machine, however, scarcely developed more than a third of the efficiency which should be possible. It is interesting to note that the first fresh meat shipment arrived in London from Australia in a vessel refrigerated by a dense air refrigeration machine.

At the present time the compression machine is more largely used than either the absorption or the dense air type of apparatus in ice making and in general refrigeration practice. The future will undoubtedly, however, see the increasing development of all types of small refrigerating plants designed for specific purposes. The household division of this exploitation is, moreover, the smaller part notwithstanding the fact that it has been the first to appeal to the public. Hospitals, grocery stores, candy shops, drug stores, lunch rooms, restaurants, florist shops, meat shops, delicatessen stores, fruit shops, trucks, and refrigerator cars are all potential users of small refrigeration machines, since ice will not be able to compete in price or convenience with refrigeration supplied by the small machines.

The Chemist in Refrigeration

To recapitulate somewhat, it was the chemist, Dr. Cullen, who discovered the vacuum system of ice making. The chemist, Priestley, moreover, discovered the extreme solubility of ammonia in water, thus providing the basis for the water-ammonia absorption machines, and chemistry has developed the solid adsorbent and absorbent. Numerous chemists, of course, have been

responsible for the development of the various refrigerants which have been used, such as ammonia, sulfur dioxide, carbon dioxide, ethyl ether, methyl ether, methyl chloride, ethyl chloride, and the hydrocarbons, some of which are now used in small machines. The chemist has had to provide the oils for the complex lubrication problems which have arisen in the refrigeration field during the past fifty years. He has studied and minimized the corrosion due to the calcium chloride used as a "brine" or for transferring refrigeration, perfected protective paints or coatings for metal surfaces, and improved the quality of all the materials entering into the improved design of all refrigeration machinery.

Already the modern chemist has added two new absorbent substances especially suited to refrigeration, an adsorbent or solid substance capable of condensing a vapor by adhesion of the vapor molecules to its enormous surface, and the other a solid absorbent for ammonia which combines greater economy than the water-ammonia system in operation with simplicity of apparatus. There are, however, still special problems by the score which will arise in the course of the accelerated growth of mechanical refrigeration during the next few decades. For the solution of these problems, men of science will be called upon continually to exercise that ingenuity and persistent effort which have already accomplished so much in this field.

Reading References

Cooper, Madison. Practical Cold Storage. Nickerson and Collins Co., Chicago, Ill., 1905.

Ewing, J. A. The Mechanical Production of Cold. The Cambridge University Press, Cambridge, Eng., 1921.

Green, Arthur M., Jr. The Elements of Refrigeration. John Wiley and Sons, New York, 1919.

Siebel, J. E. Compendium of Mechanical Refrigeration and Engineering. Nickerson and Collins Co., Chicago, Ill., 1911.

Starr, J. E. Practical Refrigerating Engineers Pocketbook. Nickerson and Collins Co., Chicago, Ill., 1922.

Wallis-Taylor. Refrigeration, Cold Storage and Ice Making. Crosby Lockwood and Son, London, 1920.

History of Refrigeration. Ice and Refrigeration, Vol. 67 (1924), pages 33, 110, 181, 227, 328, 428; also see concluding articles in monthly issues of 1925.

CHAPTER XX

RUST-RESISTING METALS

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Vice President, Electro Metallurgical Company

Chemistry has contributed almost incomparably to the progress of civilization through the development of new products from nature's store of materials. While new compositions of matter have enabled man to diversify and accelerate his activities greatly, the forces of nature continue to undo his handiwork. Physical manifestations of these forces befall us occasionally with extreme rapidity and awful destruction in the form of earthquakes, tornadoes, and similar widespread disturbances; but nature resorts also to chemical methods of attack which operate continuously though more slowly and to an extent that is little realized. A significant example of the latter type of destruction is the corrosion of metals. This is one of the successful results of nature's efforts to turn back to their natural and stable form some of the materials that applied chemistry has given to the service of man.

The literal meaning of corrosion is "eating away gradually." As applied to metals, however, chemists think of corrosion as the alteration of a metal by chemical action. It is predominantly a surface phenomenon. The most commonly observed examples of corrosion result from the combined attack of the oxygen and the ever-present moisture of the air, and of these

ordinary iron rust and the so-called verdigris on articles of copper, brass, and bronze are the best illustrations.

The Metals of Antiquity

The survival of a variety of metallic implements and ornaments has preserved for us a knowledge of the metals of antiquity. Exceptional purity in some instances and in others the protective coatings that have resulted from corrosion appear to explain their escape from total disintegration. Gold and silver ornaments are among the most widely found relics of the ancient artisan, no doubt because the occurrence of these metals in the native state enabled primitive man to fashion them with a minimum of skill and obviously because their noble nature has preserved them from attack. Next came meteoric iron and native copper for useful and ornamental articles, and these were followed by the bronzes, the development of which required a higher degree of experience because of their more involved metallurgy. Later still the iron age began, aided by a growing knowledge of the reduction of ores, and it appears to be accepted that iron implements of general utility had largely superseded those of bronze by about 1200 B. C., at least in some countries.

Iron and steel possess such superior mechanical properties as compared with copper, the bronzes, and other less corrodible nonferrous metals, and they are produced so much more cheaply and are so much more readily worked that it is extremely unfortunate that these most important metals are the least resistant to the corroding influences of the atmosphere. The annual wastage of iron and steel through corrosion has been estimated by Sir Robert Hadfield at the enormous figure of over $3,000,000,000, all contributory factors being

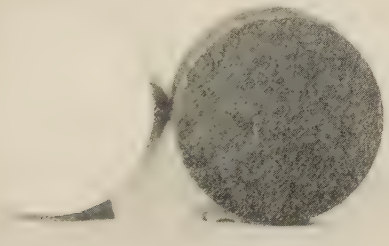
considered, including the relatively large quantities of coal required in the production of the wasted iron and steel. However approximate this figure, one does not have to stretch the imagination to appreciate that huge savings await the development of methods by which the life of iron and steel may be even slightly prolonged, and that an effective remedy for this particular type of destruction offers one of the greatest possibilities for the conservation of our natural resources.

Electrochemical Theory of Corrosion

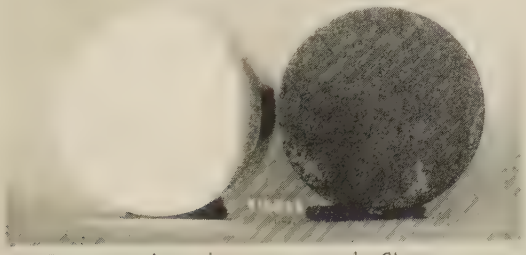
Engineers and scientists in the past have devoted more attention to other problems involving metals than to corrosion. Fortunately, more rapid progress has followed the increased and more systematic work of practical and scientific investigators during the past generation, and although their efforts have not led to unanimity as to the full explanation of corrosion, what is known as the electrochemical theory has become established on a fairly firm basis.

All are familiar with the fact that when two dissimilar metals are placed in a solution of an acid or a salt a difference of electrical potential is established which is termed the voltage of the cell. However, it is not so generally known that all metals have definite though different tendencies to dissolve in such solutions even when extremely dilute, as a result of which a difference in electrical pressure (voltage) is set up. On establishing a complete circuit, a current of electricity flows between the two metals and through the solution, but it is possible for this to occur only at the expense of one of the metals, which corrodes and passes into solution, thus converting chemical into electrical energy. The more readily soluble metal is said to be

a. Both specimens in the polished condition.



b. Specimens after 76 hours exposure to salt spray. Rust not removed.



c. Same as b with rust removed. Shows pitting of the steel.

Fig. 1. Example of the effect of salt spray on plain carbon steel and a high-chromium alloy. The steel is on the right in the pictures. The original bars were 2 inches in diameter.

electropositive to the less soluble metal, which is classed as electronegative.

Commercial irons and steels invariably contain more than one constituent, sometimes only microscopic in size, but always present as impurities and as compounds of iron with carbon and other elements. These different constituents act as dissimilar metals, the purer portions of the iron generally being electropositive to the less pure portions. In the presence of moisture and oxygen, electric cells are set up which carry the iron into solution, and this dissolved iron in contact with the electronegative constituents then becomes oxidized to iron hydrate and subsequently to a relatively porous iron oxide. The iron rust is porous enough to permit the access of oxygen, which enables these minute galvanic cells to function continuously. Iron rust therefore does not serve as a protective coatting; on the contrary, it facilitates subsequent corrosion. The accompanying diagram will serve to visualize the preceding necessarily brief outline, incomplete as to some details, of the electrochemical theory as affecting iron and steel.

Factors Influencing Corrosion

Of the many factors that are known to accelerate the corrosion of metals, some of the most important are: the contact of dissimilar metals, as exemplified in the unsuccessful attempt to sheath part of the steel schooner Sea Call with monel metal; the presence of active oxygen and almost any chemical in the surrounding medium; nonuniformity of the metal, whether due to impurities or to segregation; internal stresses in metals; stray electric currents, which have often assisted in the destruction of water mains and street

railway tracks; and elevated temperatures. The three principal means employed to prevent or retard corrosion are: the use of protective coatings; neutralization or removal of the active elements in the surrounding medium, as in the treatment of corrosive waters with alkaline compounds; and counteracting electrochemical expedients, such as the introduction of metallic zinc into steam boilers.

Corrosion of Iron and Steel

With the foregoing statements in mind it may be readily understood why the steel structures and other metals subject to exposure corrode so much more rapidly in the neighborhood of our industrial centers than in atmospheres that are unpolluted. The chief offenders are the gaseous compounds of sulfur which result from the burning of large quantities of coal. In addition to the increasing difficulties from atmospheric corrosion entailed by the expansion of our manufacturing industries, modern chemical engineering imposes other and even more severe conditions upon its structural materials in two directions—resistance to high temperature and resistance to a large variety of powerful chemicals—both of which agencies are among the most active promoters of corrosion. The electrochemical theory does not lend encouragement to the making of any single metal or combination of metals resistant to attack in all corroding media.

Iron and steel are so susceptible to corrosion that it is chiefly for this reason the more costly metals and innumerable alloys of copper, tin, lead, and zinc are still largely employed. This susceptibility also explains the increasing use of the more modern metals, nickel and aluminium, although each of the above-

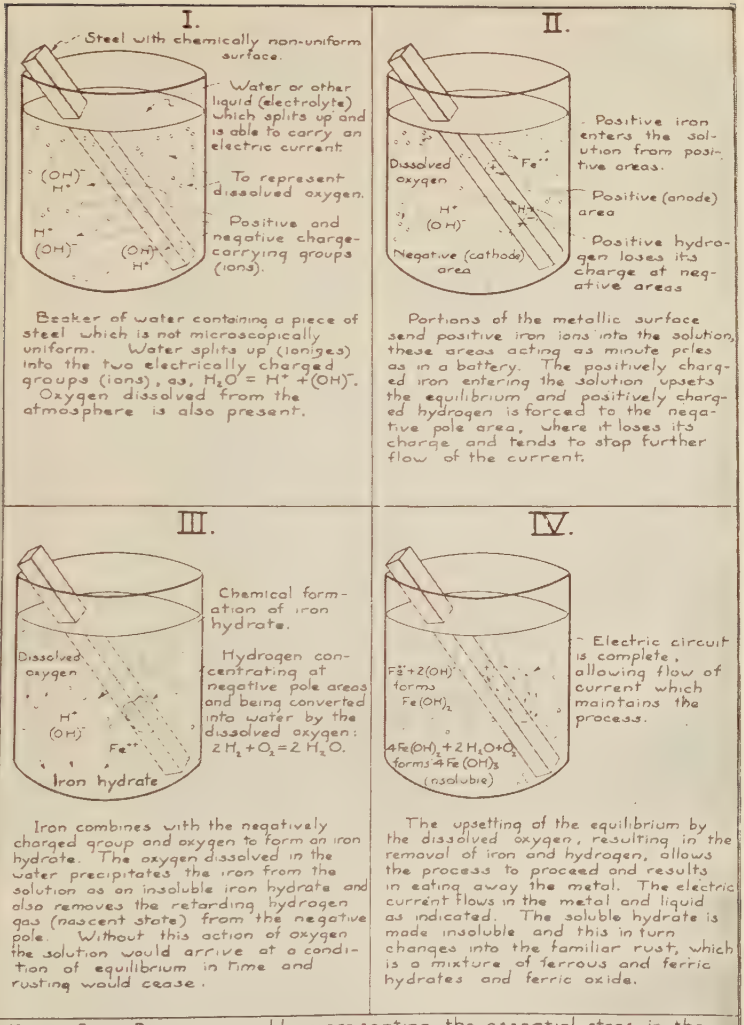

I.
Steel with chemically non-uniform surface.
Water or other liquid (electrolyte) which splits up and is able to carry an electric current.
To represent dissolved oxygen.
Positive and negative charge-carrying groups (ions).
(OH)⁻
H⁺
H⁺
(OH)⁻
(OH)⁻
H⁺
Beaker of water containing a piece of steel which is not microscopically uniform. Water splits up (ionizes) into the two electrically charged groups (ions), as, $H_2O = H^+ + (OH)^-$. Oxygen dissolved from the atmosphere is also present.
II.
Dissolved oxygen
Fe⁺⁺
H⁺
(OH)⁻
H⁺
Negative (cathode) area
Positive iron enters the solution from positive areas.
Positive (anode) area
Positive hydrogen loses its charge at negative areas
Portions of the metallic surface send positive iron ions into the solution, these areas acting as minute poles as in a battery. The positively charged iron entering the solution upsets the equilibrium and positively charged hydrogen is forced to the negative pole area, where it loses its charge and tends to stop further flow of the current.
III.
Dissolved oxygen
H⁺
(OH)⁻
Fe⁺⁺
Iron hydrate
Chemical formation of iron hydrate.
Hydrogen concentrating at negative pole areas and being converted into water by the dissolved oxygen: $2H_2 + O_2 = 2H_2O$.
Iron combines with the negatively charged group and oxygen to form an iron hydrate. The oxygen dissolved in the water precipitates the iron from the solution as an insoluble iron hydrate and also removes the retarding hydrogen gas (nascent state) from the negative pole. Without this action of oxygen the solution would arrive at a condition of equilibrium in time and rusting would cease.
IV.
$Fe^{++} + 2(OH)^-$ forms $Fe(OH)_2$
$4Fe(OH)_2 + 2H_2O + O_2$ forms $4Fe(OH)_3$ (insoluble)
Electric circuit is complete, allowing flow of current which maintains the process.
The upsetting of the equilibrium by the dissolved oxygen, resulting in the removal of iron and hydrogen, allows the process to proceed and results in eating away the metal. The electric current flows in the metal and liquid as indicated. The soluble hydrate is made insoluble and this in turn changes into the familiar rust, which is a mixture of ferrous and ferric hydrates and ferric oxide.

Figure 2. Diagram roughly representing the essential steps in the rusting of steel as explained by the electrochemical theory. While the phenomena are instantaneous and coincident and the reacting elements almost infinitely small, the process has been divided into steps and idealized to clarify the theory. The steel sample is represented as being heterogeneous.

mentioned metals has other specific properties which render it most suitable for certain purposes. Indeed, some of these metals find their largest use in the various forms of plating given to iron and steel as a means of protection.

Nonferrous Metals and Alloys

It has been explained why iron rust permits progressive corrosion. In contrast to iron, several of the above-mentioned metals, soon after exposure to the air, develop adherent and sufficiently impervious films to exclude or retard entrance of the very agencies which form them, and corrosion virtually ceases. On tin and aluminium the films are extremely durable, and being transparent they impair the metallic luster little if at all. The film on nickel under ordinary conditions is practically unnoticeable; hence the enduring brightness of the ordinary objects of iron, copper, and brass which have been perfectly nickel-plated. Recent commercial developments in the art of electroplating with chromium—a hard metal extremely resistant to atmospheric corrosion—hold out great encouragement for this method of protecting less resistant metals. The green carbonate of copper accounts for the beauty of old roofs and other architectural trim finished in that metal. Zinc and tin form protective and durable alloys on the surfaces of iron and steel and prolong their life in the atmosphere. The objects are most commonly dipped into molten zinc or tin, sheets thus treated constituting the commercial galvanized iron and tin plate.

Many uses of these nonferrous corrosion-resisting metals and alloys are so familiar as to pass unnoticed. For example among the pure metals are the tin, lead,

and aluminium foils; shingles, rain spouts, and woven-wire screens of copper; shingles, nails, and builder's hardware of zinc; lead pipe and lead-covered electric cables—all of these are familiar objects.

The cooking and preserving of food introduces the element of chemical attack. Vegetable and fruit acids are appreciably corrosive to many metals, but the substances most employed in the culinary art are not strongly corrosive, and aluminium vessels have largely replaced the copper and the tin-clad steel utensils of earlier times. Those of the highest grade are of nickel, the use of which is increasing. Cans of soft steel coated with tin are almost universally used for the preservation of fruits, vegetables, meats, and fish in the widest variety, and in this field tin is supreme.

The metallic equipment required in the manufacture, storage, and transportation of chemically active substances must possess exceptional resistance to corrosion. Corrosion is almost always in progress, however slowly, and discoloration of the product by the dissolving metal is usually objectionable. For this reason copper has been largely replaced by aluminium, the distillation of acetic acid being one of its few important surviving uses. Copper and iron being highly resistant to alkalies, interest is focused therefore on the acid resistance of the remaining nonferrous metals and their alloys.

Lead was one of the earliest metals to be employed in chemical manufacture because of its remarkable resistance to corrosion by sulfuric acid. Its soft nature precludes its use in some types of machinery, although its application is considerably extended through the hardening effect brought about by the addition of antimony.

As the purity of aluminium and the skill in its fabri-

cation have increased, this metal has found several applications in chemical industry, and owing to very recent improvements in quality its use is likely to be still further expanded.

Copper Alloys

Copper alloys generally excel pure copper in corrosion resistance. Among these are certain of the zinc-copper alloys (brasses) and the tin-copper alloys (bronzes), also the bronzes containing manganese or aluminium. In some of the important aluminium bronzes that element is the predominating constituent. Many of these combinations have excellent mechanical properties and at the same time serve very useful specific purposes as acid-resisting alloys. The bronzes excel the brasses in corrosion resistance, and the highest resistance to acids is found in the alloys which contain in addition to copper and tin either nickel, iron, manganese, zinc, or lead. Propellers, marine valves and condensers, mine pumps, and large valves for important hydraulic service offer leading examples.

Monel metal is an alloy of nickel and copper in the same proportion as these metals exist in the particular nickel-copper ore from which it is produced, a ratio of approximately two to one; it excels most of the bronzes in resistance to all forms of corrosion and finds a wide field of application because it can be readily cast, rolled, and drawn. The castings enter the same fields as those mentioned for bronze, while the wrought forms appear in marine piping and condenser tubes, dyeing, bleaching, and laundry machinery, and dairy and restaurant equipment.

Nickel and nickel alloys of the monel type are fairly resistant to scaling and oxidation at elevated tempera-

tures, for which reason they find additional applications in the industries. To render the surface of iron and steel nonscaling at a full red-heat, aluminium is alloyed as a coating by a special treatment known as calorizing, which depends on a film of aluminium oxide for resistance to oxidation.

The electrochemical theory of corrosion suggests that one way to increase the resistance of iron is to eliminate the impurities, and certain brands of iron are pure enough to display a marked improvement in their resistance to several forms of corrosion. Proceeding in the opposite direction, it has been found that the addition of certain elements so materially alters the electrochemical properties of the iron that corrosive action is either suppressed or much retarded. For example, copper up to 0.25 per cent greatly inhibits atmospheric corrosion of steel, while a silicon content approximating 15 per cent gives iron a remarkable immunity to attack by acids. As materials for resisting atmospheric corrosion, irons of exceptional purity and the copper-bearing steels represent two striking metallurgical achievements of the present generation.

Effect of Chromium

Chromium not only increases the immunity to corrosion of iron or steel when added in suitable proportions, but at the same time it improves their mechanical properties in several important respects. By varying the proportions of chromium and of carbon, and applying correct heat-treatment when necessary, a series of useful metals can be produced, each with its individual mechanical properties but all showing exceptional powers of resistance to corrosion.

A rational explanation of the precise manner in

which chromium retards corrosion would undoubtedly hasten progress. However, present knowledge supports some ideas as reasonably tenable. It has been established that chromium will dissolve in pure iron, forming iron-chromium alloys of extremely low corrodibility. Chromium also combines with the carbon always present in steel and forms a group of compounds known as iron-chromium carbides. However, by heating the steel to a bright red heat, these carbides may be made to dissolve in the iron-chromium alloys and lose their identity. By rapid quenching this state of solution may be largely preserved at ordinary temperatures. If the steel is allowed to cool slowly, the carbides precipitate from the solution and by so doing not only diminish the proportion of chromium available for ennobling of the iron, but they may actually function as elements electronegative to the iron-chromium alloys and thereby stimulate corrosion. In order to impart stainlessness to iron-chromium alloys of appreciable carbon content, the necessity of heat-treatment is recognized in practice.

Stainless Steels

The combination of high strength and corrosion resistance has introduced stainless steels into widespread engineering applications. Most of them contain between 12 and 14 per cent chromium and 0.25 to 0.40 per cent carbon. This range of chromium imparts sufficient noncorrodibility for a great variety of purposes, and this variation of carbon permits hardening and tempering within wide limits of physical properties. Indeed, this composition makes available a nonrusting material which is amenable to modern methods

of fabrication and possesses much higher strength and abrasive resistance than ordinary steel.

Rustless Iron

A somewhat more recent commercial development is rustless iron. It is of the same family, having substantially the same limits of chromium, but it differs in the important respect of having a much lower carbon content, preferably less than 0.10 per cent. With the foregoing explanation as to the effect of chromium carbides on corrosion, it will be clear why stainless steel requires a quenching or hardening treatment to induce the condition of maximum noncorrodibility. On the other hand, so low is the carbon content of rustless iron that a very much larger proportion of the chromium is dissolved in the iron, relatively few carbides are present, and hence rustless iron is rust-resisting without heat-treatment. Being softer than stainless steel and more readily rolled, forged, and cold-worked, and not requiring heat-treatment of finished forms, articles of rustless iron can be more cheaply produced. It must be borne in mind, however, that rustless iron cannot be given many of the exceptional physical properties of stainless steel, because of its low carbon content, and the two materials therefore have separate fields of application.

The imagination of a metallurgist is not necessary to conceive the widespread uses awaiting materials which possess the high strength and noncorrodibility of these alloys—in fact, without an engineering material having such a combination of properties the desired goal would scarcely be in sight. It is therefore not surprising that the applications have become greatly diversified since their recent commercial introduction.

These alloys are rendering valuable service in our homes and on the farm; in our automobiles and sporting equipment; in many of our manufacturing industries; and in our carriers on land and sea. Although so diversified in application, the extent of their substitution for materials now employed has not been great, and therefore the tonnage of steel involved is only beginning to be appreciable.

To be strictly nonrusting, stainless steel and rustless iron must be exceptionally well made. They must be thoroughly deoxidized and free from foreign inclusions and scale, or rusting will inevitably occur. The making of entirely satisfactory materials is now a practicable, commercial operation. Extreme segregation, slag or other nonmetallic inclusions, or other evidence of poorly made material explain the failures in service that have occasionally been observed.

Another group of commercial iron-chromium alloys embraces a wide range of chromium upwards of 20 per cent, with carbon content adjusted to give the desired physical properties. Nonrusting under even more exacting conditions than are rustless iron and stainless steel, they are also invulnerable to attack by a greater variety of corrosive substances. The attaining of high temperatures at which it is desirable to conduct certain industrial processes has been barred by lack of reasonably inexpensive metals or alloys that will not rapidly deteriorate through the formation of a loose scale (oxidation) above a bright red heat. It is in this somewhat more spectacular field that the iron-chromium alloys containing upwards of 20 per cent chromium are the most prominent, and they are rapidly reaching a high degree of engineering development. The thin coat acquired on the surface of these alloys is so tough and adherent that an almost

indefinite life is assured under oxidizing conditions at temperatures up to 1100° C. These applications also promote conservation by permitting new chemical processes to be carried on and by making some of those now in use more efficient.

The addition of appreciable nickel to rustless iron, stainless steel, or the iron-chromium alloys of high chromium content enhances their resistance to corrosion by some of the important chemical substances, but in some cases the corrosion resistance is diminished. For a number of years nickel-chromium and nickel-chromium-iron alloys in which the nickel is largely predominant have been available commercially. Although these alloys admirably withstand most atmospheric conditions, as well as attack by a considerable variety of chemical reagents, their chief application has been in such arts as can take advantage of their excellent combination of oxidation resistance and high strength at elevated temperatures.

Search for the Ideal Metal

Almost all the major endeavors to improve man's status in respect to material things have involved the question of economics. Broadly viewed, the corrosion problem presents no exception. What combination of qualities in a metal should we choose as ideal from a strictly utilitarian standpoint? Essentially, strength and permanence; preferably, also luster. At present the element chromium appears to offer the most hopeful prospects. With increasing scientific knowledge and greater skill in practical manufacture, chromium irons and steels of the type described—to mention a development in the ferrous field alone—will be so much more economically produced that inevitably their

use will be recognized as necessary in many common applications. But our present knowledge of the distribution of nature's raw materials leads us to wonder what will be the ultimate solution of the corrosion problem.

Think of the very recent changes in our fundamental conception of matter! Further scientific progress in this direction may be expected to assist commercial endeavor enormously. As tools of research, the metallurgical microscope and the more recently devised X-ray spectroscope will undoubtedly modify our ideas of the constitution of metals and contribute to practical attainment.

Truly, the future may be viewed much more hopefully than was warranted even ten years ago. A period of new development has been entered which permits visualization of nonrusting metals contributing their share towards conserving our resources, expanding our activities, and better pleasing our esthetic sense.

Reading References

Aitchison. The Theory of the Corrosion of Steel. Trans. Iron and Steel Inst., Vol. 1, 1916.

Cushman and Gardner. The Corrosion and Preservation of Iron and Steel. McGraw-Hill Book Co., 1910.

Evans. Corrosion of Metals. Arnold & Co., London, 1924.

MacQuigg. Some Commercial Alloys of Iron, Chromium and Carbon in the Higher Chromium Ranges. Trans. American Inst. Mining and Metallurgical Engineers, Vol. 69, 1923.

Monypenny. Stainless Steel, with Particular Reference to the Milder Varieties. Trans. American Inst. Mining and Metallurgical Engineers, Vol. 70, 1924.

Pollitt. The Causes and Prevention of Corrosion. D. Van Nostrand Company, 1923.

Van Patten. Corrosion Bibliography. Marblehead, Mass., 1923.

Transactions of the Faraday Society, Vol. 19, Part 1, July, 1923, pp. 159-230. Valuable articles by Hatfield, Monypenny, Kayser, Evans, Arnott and others.

Corrosion-Resistant, Heat-Resistant and Electrical-Resistant Alloys. A symposium held at the 1924 Annual Meeting of the American Society for Testing Materials.

CHAPTER XXI

SOAP—CLEANLINESS THROUGH CHEMISTRY

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Soap is mentioned in the Bible and in early Latin writings. Regardless of the actual methods by which such "soaps" were prepared, it is probable that they all contained some real soap, or at least produced some soap when used to cleanse greasy surfaces. Improvement in soap manufacture was slow and gradual until in the early part of the last century a French chemist, Chevreul, through classical researches determined the true chemical character of fats, fatty oils, and soaps, thus laying a firm foundation on which the modern soap industry is built.

I remember distinctly, as a small boy in the country, seeing the soap-making process carried out as it no doubt had been for hundreds of years and still may be in some remote districts. This was a springtime operation and was calculated to utilize the fat and grease saved from cooking and the wood ashes collected from the household stoves and fireplaces during a long winter. An old cask with one head was selected. Numerous auger holes were bored in the head and the cask was then filled with alternate layers of straw and mixed lime and wood ashes. The cask was placed on a raised, slanting, grooved board. From time to time a pail of water was poured upon the contents of the cask, and eventually a brownish liquid began to emerge

and was collected in a pail and transferred to an iron pot. A chemical action took place which converted *potash,* the chief ingredient of the wood ashes, into *caustic potash;* and the brownish liquid or lye was then boiled in an open iron pot over a fire, out of doors, with the fat or grease until the experienced eye of the soap maker looked upon it as finished. The fire was then allowed to go out and the contents of the pot left to chill to a solid mass, after which it was cut into bars of odd shapes which were none too firm. The quality of the soap depended on the skill and luck of the operator. These old-fashioned soap boilers were rule-of-thumb chemists though they did not know it.

The old-time professional soap boiler did just what I have described, and little real improvement came in soap making until the chemistry of the process became better understood, since which further progress has come hand in hand with chemical disclosures.

Speaking chemically, soap is a salt of a metal with one of the higher fatty acids. It is usually a salt of an alkaline metal, sodium or potassium, and mixed fatty acids, as the individual unmixed fatty acids are not readily obtainable.

Saponification

Soaps are commonly made by the chemical action of a caustic alkali, as sodium hydroxide, on a fat or fatty oil. By this action, known as saponification, there are made at the same time not only soap but also a by-product known as glycerol.

Tristearine (Fat)		Caustic Soda		Soap		Glycerol
$(C_{17}H_{35}COO)_3C_3H_5$	+	$3NaOH$	=	$3C_{17}H_{35}COONa$	+	$C_3H_5(OH)_3$

Neither glycerol nor fatty acid exists as such in fats though the glycerides, of which fats and fatty oils con-

sist, hold both of these potentially present and yield them on saponification.

Alkali

The old-time soap maker was forced to make his own caustic potash from wood ashes, or "potashes," and lime. Some of the largest soap makers still find it advantageous and economical to make their own lye in the form of caustic soda by causticizing soda ash, anhydrous sodium carbonate obtained from the large alkali makers. The sodium carbonate dissolved in water is boiled and agitated with an excess of freshly slaked lime with the formation of soluble caustic soda and insoluble calcium carbonate:

Sodium Carbonate		Slaked Lime		Caustic Soda	Calcium Carbonate
Na_2CO_3	+	$Ca(OH)_2$	=	$2NaOH$	+ $CaCO_3$

This reaction can be carried out over a wide range of concentration. When much water is present, calcium carbonate, one of the end products, is the only insoluble substance present and the causticization proceeds until practically all the sodium carbonate is replaced by caustic soda, the calcium carbonate settling out. In the higher concentrations the calcium carbonate is not the only insoluble substance present, as the slaked lime under this condition is very much less soluble and the reaction slows up and comes to a balance before all the sodium carbonate has been converted to caustic soda. The makers of solid caustic soda usually operate in the higher concentrations and get rid of this excess of sodium carbonate by boiling the solution down until it is nearly strong enough to solidify on cooling. The sodium carbonate is then almost insoluble and settles out readily. The soap

Courtesy, Colgate & Co.

One of the Large Soap Pans While Boiling. These Pans Hold About a Million Pounds of Soap.

maker usually prefers to operate in sufficient dilution to give him a lye with little remaining carbonate. He is thus saved unnecessary and expensive evaporation, and as his lye is used where made he does not have to pay freight on the excess water.

Soap Making

There are several methods of making soap which are more or less in vogue. A description of the one most commonly used will give a good idea of the chemistry involved. The fat in melted condition is pumped into the "kettle" or "soap pan," where it is boiled up with open steam which serves both to heat and to agitate. The pans are frequently large enough to hold a million pounds of soap. The practice of heating the pans by fire has been discontinued in all modern factories. They are now provided with open steam jets which discharge into the soap the water of condensation, which is very helpful in saponification, and also with large closed steam coils, the condensed water from which is conducted away from the pans. Steam heating gives the soap boiler perfect control through steam valves.

During saponification the contents of the pan are kept boiling so as to promote chemical action and thorough mixing. The lye, consisting of from 10 to 20 per cent solution of caustic soda, is run in rapidly but so that a large excess of uncombined alkali is avoided at any time. The saponification proceeds smoothly almost as fast as the lye can be run into the pan. It is easy for the operator to tell if the alkali is being taken up, and towards the end of the process the lye is run in more slowly. After there is an excess of lye present the soap is thoroughly boiled up to

insure complete saponification. The soap is then grained by the addition of salt, or better, a strong salt solution. Soap is almost insoluble in either strong caustic soda or strong salt solution and an addition of sufficient of either of these grains it so that it separates in large insoluble curds. The boiling is now continued by means of the closed steam coil. Any impurities that may have been present in the fat are largely destroyed by this boiling with caustic soda. The glycerol formed by the saponification goes into solution in the lye and should any fat have escaped saponification up to this time it is converted into soap during this boiling.

When the steam is turned off, the lye layer, containing most of the excess alkali, salt, and glycerol, being heavier than the soap, settles to the bottom of the pan and is removed. It is boiled with fresh stock and in this way the excess alkali is not lost but is used in making more soap. The spent lye is then sent to the glycerol department for the recovery of glycerol.

The soap left in the pan is boiled again with salt solution or fresh lye, and further lyes are removed, the objects attained by this being the complete removal of soluble or destructible impurities, the separation of insoluble impurities, the more thorough recovery of glycerol, and the insuring of complete saponification. Practice may vary in details without affecting the principles involved. After the final lye is removed from the pan, water is slowly run in while the soap is boiled up with open steam. The effect of this is gradually to dilute the lye surrounding the soap curds until the solubility of soap in it becomes greater and greater. At the same time the soap curds take up a little more water and become very thin in consistency. The contents of the pan at this time still consist of a "two

phase system," a lye phase diluted to the point where it contains an appreciable amount of dissolved soap in addition to nearly all of the salt, glycerol, and excess alkali still present, and a soap phase which consists of almost pure soap containing a very small amount of dissolved salt and alkali. It is important not to add too much water during the settling operation as this would cause the two phases to merge into one and permit of no separation of pure soap from the salt and alkali.

When the right point is reached and the soap is at a point of minimum viscosity, the steam is shut off and a rapid separation of the two phases into two distinct layers is brought about. This separation can be produced at once in a centrifuge, or by gravity on standing. The upper layer consists of an almost perfectly pure settled soap containing about 30 per cent of water, and the lower diluted lye layer, known as "nigre," contains practically all the impurities, as salt and alkali, and about one-fifth of the soap in solution. Each of these phases or layers is absolutely homogeneous throughout except for local influences and there are but two phases at this stage, notwithstanding a common belief that there is also a lye layer that is practically free from dissolved soap. During the time that is necessary for gravity settling, the contents of the pan become somewhat cooled and the nigre or lower phase which separated when hot suffers a change due to the cooling, the solvent properties of the dilute lye becoming less. This brings about a separation of some of the soap of the nigre from the cooled lye, a small amount of which then settles to the bottom of the pan, giving rise to the belief that the settling involves a third, clear lye phase.

When soap is kept hot it is in a liquid state and the pure liquid settled soap may be pumped off and sent through pipes to any part of the factory. This is a great saving in labor over what would be required to dip the soap out or move it about by other means.

Glycerol Recovery

The various spent lyes removed from the soap pan are treated for the recovery of the excess alkali they contain and are then treated with a salt such as ferric chloride or aluminium sulfate which forms insoluble soaps. In this way any soap remaining dissolved in the spent lye is precipitated as an insoluble soap and is removed by filtration. These insoluble soaps, being gelatinous in nature, form coagulants which enclose other suspended impurities, thus aiding complete clarification. The lye, now neutral and clear, is evaporated in large multiple effect evaporators under reduced pressure. Salt crystallizes out, is separated from the concentrated glycerol lye, and removed to the soap department to be used to salt out soap again. By further concentration a soap-lye crude glycerol is obtained which contains approximately 80 per cent glycerol. This is subjected to distillation with steam in vacuum stills and yields the so-called "dynamite glycerine" of commerce from which nitroglycerine is made. Further distillations produce a very pure high-grade glycerol, the "C. P. Glycerine" of commerce.

One hundred pounds of any of the common fats when pure and neutral will give ten pounds or more of glycerol. The glycerol yield is an important factor in soap making. The best practice approximates the theoretical yield.

Acid Saponification

Owing to the value of the glycerol produced during saponification, other methods than that described above have been devised for making soap with the idea of increasing the yield or simplifying the extraction of glycerol. Probably the simplest and best of these is the Twitchell process, devised by an American chemist. The saponification is brought about by gently boiling the fat or oil with water containing a small amount of sulfuric acid and a fraction of a per cent of a catalyst, a sulfonic acid, which results in a direct formation of fatty acids and glycerol. During the saponification by means of acid, each fatty molecule is split up together with three molecules of water, and the immediate results of this splitting action rearrange themselves with the formation of three molecules of fatty acid and one of glycerol.

Fat		Water		Fatty Acid		Glycerol
$R\text{-}COO\text{-}CH_2$		OH H				CH_2OH
$R\text{-}COO\text{-}CH$	+	OH H	=	$3R\text{-}COOH$	+	$CH\ OH$
$R\text{-}COO\text{-}CH_2$		OH H				CH_2OH

The catalyst suffers no permanent change in the reaction. The glycerol is dissolved in the acid water and may easily be recovered by the neutralization of the acids in the water layer with lime, filtration, evaporation, and distillation. The crude glycerol obtained by this process is free from dissolved salt and a number of other impurities present in soap-lye crude glycerol. The fatty acids obtained by the Twitchell saponification may be neutralized with caustic soda or even by sodium carbonate solution and made into soap preferably by the settled soap process, the lyes in this case being practically free from glycerol.

In an acid saponification it is necessary to observe certain precautions to exclude the air from the fatty acids during boiling and to avoid their coming in contact with iron. Neglect of these precautions is apt to affect adversely the color of the fatty acids.

Lime Saponification

There is another method of making soap that is interesting from a chemical standpoint and is worth mentioning, though it involves many mechanical difficulties. By this process the fat is stirred up with a thick milk of freshly slaked lime in slight excess over the amount necessary for saponification. After stirring for a short time the mass thickens and is then allowed to stand and soon becomes solid owing to the formation of calcium soap. When this soap is broken up, the glycerol in concentrated solution may be seen all through the mass in small liquid beads. The solid soap mass must be dug out of the saponifying vessel and be finely ground so that the glycerol contained may all be exposed to a leaching process for its recovery. The ground calcium soap is repeatedly washed with hot water in which it is nearly insoluble. In this way the glycerol is dissolved out and may be obtained as a good quality crude glycerol after evaporating off the water. The extracted calcium soap is now transferred to a soap pan and is boiled up with salt and water and sodium carbonate. Under proper physical conditions the calcium soap and sodium carbonate undergo a chemical interchange with the formation of insoluble calcium carbonate and common soda soap.

Calcium Soap Sodium Carbonate Soda Soap Calcium Carbonate

$$(R\text{-}COO)_2Ca + Na_2CO_3 = 2R\text{-}COONa + CaCO_3$$

Courtesy, Colgate & Co.

Part of One of the Laundry Soap Framing Floors

There is a well-known chemical principle which causes a chemical action of this kind to continue until it is completed if one of the products of the reaction is insoluble and the others are soluble. The calcium carbonate formed is more insoluble than the calcium soap and if the calcium soap and the soda soap are not also made insoluble by the use of too much salt, the conversion into soda soap and calcium carbonate will be complete. The soap is finished by a settling as in the settled soap process, but in this case a large amount of calcium carbonate is disseminated through the nigre phase and can be removed only by diluting and filtering. This process is carried out successfully in a number of small European factories where labor is cheap, but on account of the necessity for digging out and pulverizing the solid calcium soap and the difficulty of completely removing the calcium carbonate, and the extra labor involved, the process offers no attraction to American soap makers.

The soap-making processes thus far described are common to many kinds of soaps. Differences in the final products are brought about by variations in composition or subsequent treatment.

Various Kinds of Soaps

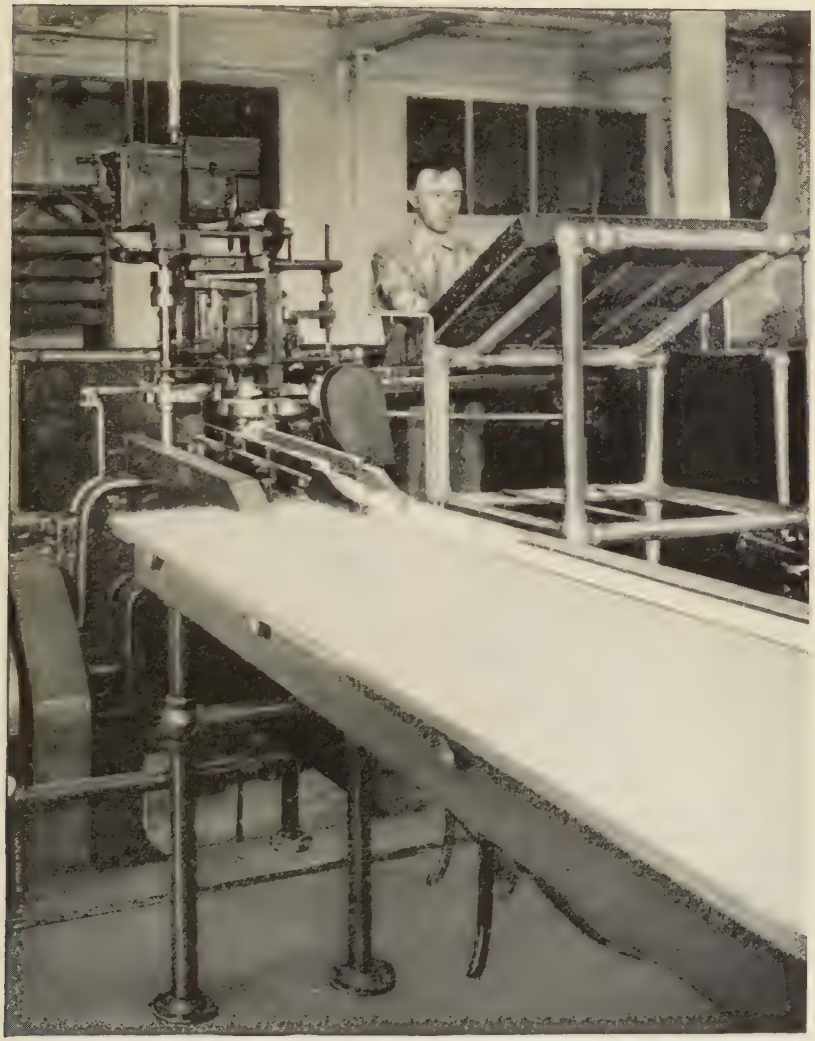
A large percentage of the soap used in the household contains a certain proportion of rosin soap mixed with the fatty soap, the object of this being to increase the solubility and sudsing qualities in cold water and to make the soap wash better under average conditions than would be possible with soap made from a hard fat like tallow without rosin soap. Coconut oil is used along with other fats and oils in making float-

ing soaps and toilet soaps to give them free lathering qualities.

Floating soap is made by beating air into molten settled soap until the aeration is sufficient to cause it to float. It is then chilled and cut into cakes.

Soaps for general household use are made by mixing some sal soda or silicate of soda into hot settled soap, letting it chill in frames, and then cutting it into bars and cakes. Household soaps which contain no sal soda or silicate of soda work well in pure soft water but, where only hard water is available and there is no suitable arrangement for softening it, the most satisfactory results can be obtained only by the use of one or both of these water-softening chemicals, either in addition to the soap or incorporated in it. The use of sal soda and silicate of soda with hard water and soap prevents an insoluble calcium or magnesium soap curd from forming and depositing on the clothes. It is for this reason that the soaps that have given the most satisfaction in hard-water districts contain silicate of soda or sal soda, and most household soaps are so made.

Toilet soap is now usually made by the settled soap process, subjecting the soap base thus obtained to drying, and machining to work it into cakes of suitable size and shape. The pure settled soap is run onto large hollow steel rolls that are cooled by water. It is chilled to a solid film by passing through a succession of these rolls of varying speeds, the soap film always adhering to the faster roll. It is cut off into ribbons which fall upon endless wire belts and are thus carried through a drying chamber provided with a strong circulation of warm dry air. In this way the soap is dried until only about 8 to 12 per cent of moisture remains, as compared with the 30 per cent



Courtesy, Colgate & Co.

Pressing Toilet Soap.

originally present in the settled soap and left in most floating and laundry bar soaps, since the rapid drying of these latter in bar form is not an easy matter.

The dried soap ribbons are mixed with some perfume material, are run through large roll mills to make the mass thoroughly homogeneous, and are then squeezed in powerful screw machines, called plodders, until a solid mass is obtained, and this is forced by great pressure to flow through a suitable nozzle, cut off into pieces of the desired weight, pressed into cakes, and wrapped. Most of this work is done by machinery.

Most laundry and toilet soaps are perfumed. This is primarily to make them more agreeable in use, although the perfume materials also exert a little preservative sweetening effect, preventing or delaying rancidity. The perfume materials used are derived mostly from flowers and plants by steam distillation and from synthetic chemicals. Many of the ingredients used in perfuming soap are similar to those used in flavoring confectionery.

Transparent Soap

The aim in making some soaps transparent is to add to their attractiveness. There are two ways of accomplishing this result, the English and the German methods. In using the former method, a pure soap containing some rosin soap is chipped and dried and then dissolved in alcohol. The excess alcohol is distilled off and any slight insoluble impurities are allowed to settle out. The clear alcoholic soap solution is then run into long molds where it is allowed to chill. The solid bars thus obtained are cut into individual blocks which are stamped into cakes and then allowed to lose their alcohol by long standing. The soap

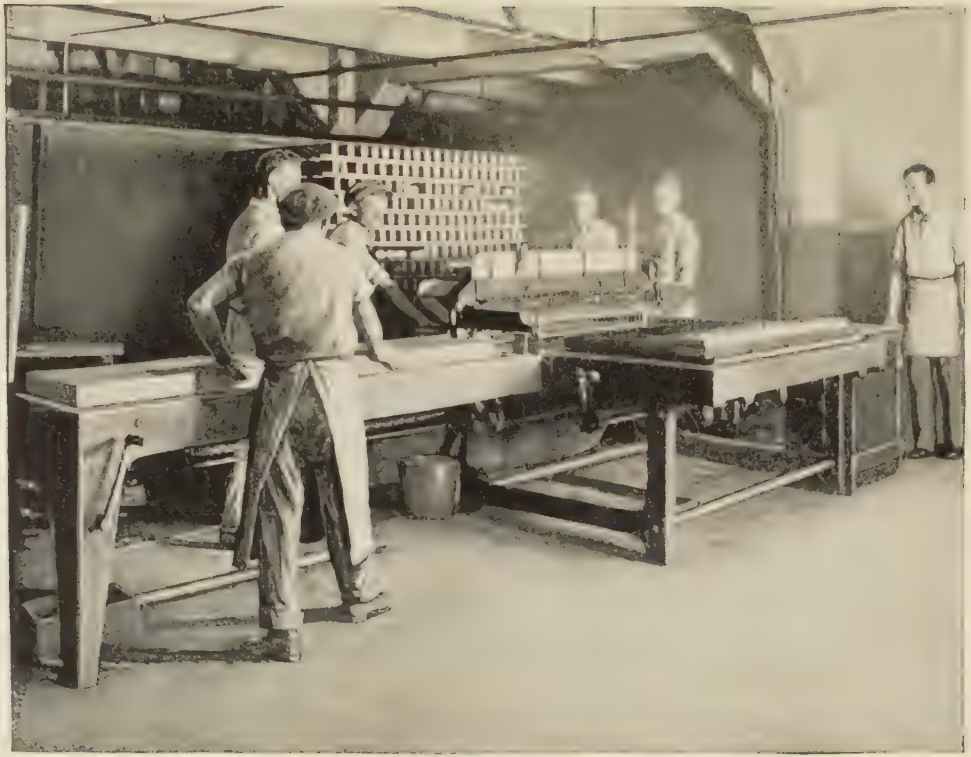
gradually becomes quite clear and transparent and in time practically devoid of water and alcohol.

The other method for making transparent soap consists in dissolving the fat or oil with just the right amount of concentrated caustic soda calculated to complete saponification, in the presence of some alcohol and concentrated sugar solution with perhaps a little glycerol. It is customary to use some castor oil in the making of these soaps, as soap made from this oil readily becomes transparent. After the soap is saponified and all the ingredients mixed, some color is added and the clear solution is poured into molds which yield bars that are later cut into cakes. The sugar transparent soaps in contrast with the first type described are not dried but contain a considerable amount of water and alcohol when sold. For this reason they waste away very rapidly in use.

There is some demand for liquid soaps. These are merely solutions of soluble soaps in water or in water and alcohol. There are comparatively few oils that are suitable for the manufacture of this class of soap, as any oil which yields an appreciable amount of stearic or palmitic or other hard soap will yield a solution which becomes gelatinous or turbid on cooling. Coconut oil is the principal oil used in these soaps. If it is the main fatty ingredient used, it is open to the objection that it leaves a characteristic disagreeable odor on the hands and produces a harsh effect on some skins.

Shaving Soap

Most soaps are made primarily for cleansing, but during recent years a large demand has grown up for shaving soaps which are calculated to facilitate the



Courtesy, Colgate & Co.

Cutting Laundry Soap

shaving operation. To accomplish this well they should lather freely in hot or cold water and give a close lasting lather that will not dry out appreciably during the time of shaving. Almost any soap can be used, but one who has used a well-made shaving soap will not voluntarily go back to an ordinary soap for this purpose. The hairs are softened by the moisture of the lather, which penetrates and is absorbed after the oil naturally on the hairs is emulsified. A good result cannot be obtained by working up a thick lather in a cup and then simply spreading it on the face. Some mechanical action is necessary to emulsify the oil on the hairs and this can best be obtained by working up the lather on the face with a brush. Contrary to a common belief, not the bulkiest lather, but the one which transmits the most moisture to the hairs is the best. A bulky lather can be obtained with ordinary toilet soap or floating soap, but it will not last and will not give a comfortable shave. Various shaving soaps are made more or less by secret formulas and by secret processes. Some of these "secrets" are common to most shaving soaps. Perhaps the most common is the use of at least some potash in the composition instead of all soda, the use of some hard fat which gives closeness to the lather, and perhaps some coconut oil soap which because of its ready solubility causes the more rapid formation of lather at the start.

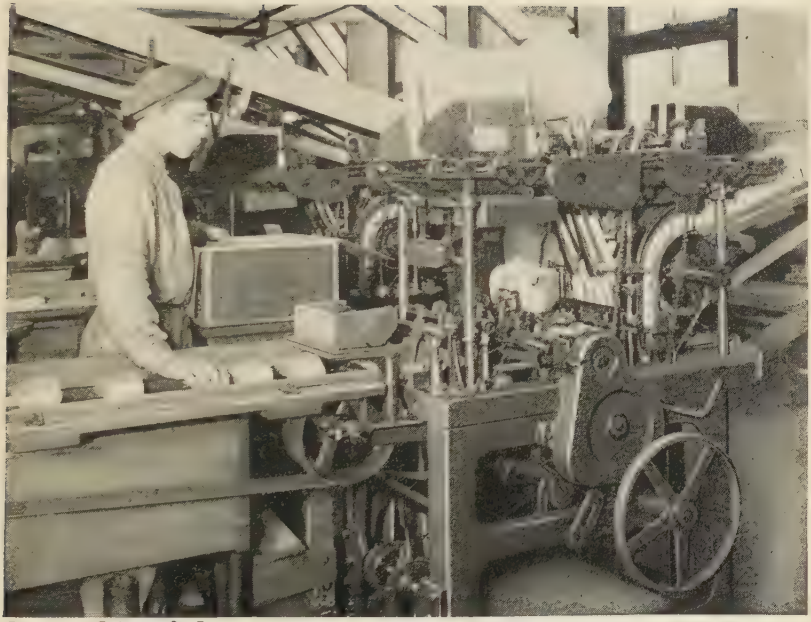
Cleansing Action of Soap

The cleansing action of soap solutions is due mainly to their low surface tension, to their slippery lubricating character, to the ease with which they form emulsions, and also to their solvent properties. Because of their low surface tension they wet readily

and spread evenly over nearly every kind of surface, and for the same reason particles of dirt that have become detached and surrounded by films of soap solution show almost no tendency to unite or to adhere to surfaces being washed, and thus remain behind in the suds or are carried away in the first rinse water. The mild alkalinity of soap solutions favors the formation of emulsions with all kinds of finely divided dirt. Some mechanical action is necessary in nearly every case, both as an aid in detaching dirt and in breaking it up into finer particles which become surrounded by soap films and are thus held in a more or less emulsified condition. The lubricating character of the solutions aids the emulsification by increasing the effectiveness of the mechanical action.

Color

Most toilet and floating soaps are made from tallow and coconut oil. These ingredients give white soaps. Palm oil gives a deep reddish orange soap when not bleached and a light brownish soap when the oil is bleached, this process usually being brought about by subjecting the oil to an oxidizing treatment as with sodium dichromate and dilute muriatic acid. Pure olive oil gives a white soap frequently called, also, Castile soap, though of late this name has been applied, whether rightly or wrongly, to some soaps which contain little or no olive oil soap. There is a poorer grade of olive oil known as "olive oil foots," or "sulfur olive oil," because it is generally recovered by extraction with carbon bisulfide from the olive residues after the better grades of oil have been removed by expressing. This material is the source of the green olive oil soaps largely used in the textile indus-



Courtesy, Colgate & Co.

Wrapping Laundry Soap.

try and also used as the base of some cheap toilet soaps. The yellowish color of many household soaps is due to their containing some rosin soap.

Chemical Characteristics of Fats

Many fats yield stearic and palmitic acids, which are saturated and solid, and oleic acid which is unsaturated and liquid at ordinary temperatures. A common though erroneous and inadequate view of fats and oils is that these are made up almost exclusively of glycerides of these three acids in different proportions. A study of the fatty acids and soaps made from them shows far more variety in their composition than could be accounted for by any such simple scheme. Oleic acid differs from a saturated acid by two hydrogen atoms less than the corresponding saturated acid. The nature of an organic body is not determined alone by the percentage of carbon, hydrogen, and oxygen contained, or by the exact number of atoms of each in a molecule, but by the exact arrangement of these atoms in the molecule, each different arrangement giving an entirely different chemical body. It is easy to see on a little inspection of possible groupings of organic bodies with as many as sixteen or eighteen carbon atoms, the number present in some fatty acids, that many different arrangements are possible.

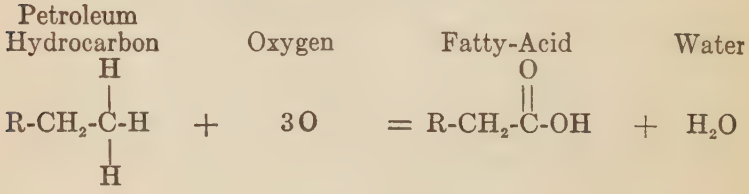
With a few exceptions, it is not at all easy to separate fatty acids one from another so as to get them in a perfectly pure state for study. Some day better methods will be devised and there is no doubt that they will lead to information that will be taken advantage of in soap making.

Hydrogenation

At times the market is such that the soap maker has free access to cheap soft oils and cannot readily get hard fats to meet his needs. The soft oils all yield unsaturated acids, and it is now possible to add hydrogen readily to these acids, giving saturated or more nearly saturated bodies which make harder soaps. This is done by agitating the oil with hydrogen in the presence of a small amount of a catalyst, as finely divided nickel, at about 185° C. In this way soft vegetable oils and whale oil are often converted on a large scale into soap fat and even into good edible products.

Possible Source of Fatty Acids

All fatty acids have a terminal grouping with a carbon atom attached to two oxygen atoms, one of which is in turn attached to a hydrogen atom. A large proportion of the petroleum oils are made up of hydrocarbons with a terminal grouping consisting of a carbon atom attached to three hydrogen atoms, forming what is known as a methyl group. Many organic bodies with a methyl group are easily oxidizable into an acid having a group such as is common to all fatty acids. If a means can be discovered to direct three atoms of oxygen so that they will attack the terminal methyl in petroleum, a fatty acid will be formed.



Courtesy, Colgate & Co.

Wrapping Toilet Soap by Machinery

Although this now seems difficult, it is not at all improbable that a catalyst will be found that will bring about this partial oxidation with air under certain favorable physical conditions. More wonderful and apparently more difficult things have been done and are now commonplace.

Distillation of Fatty Acids

Most of the fats and oils used for soap making will yield good pure soaps after thorough boiling with caustic soda, but there are some low-grade recovered greases such as garbage grease that are not suitable for making directly into soap. These greases are subjected to an acid saponification and the dark fatty acids thus obtained are then distilled in vacuum stills with steam at a high temperature. Light-colored or white acids are thus distilled over which are quite suitable for use in low-grade soaps, as they have been thoroughly purified by this treatment.

There is probably no large industry that occupies so narrow a field of chemistry that it can afford to disregard some of the problems of other industries. The industry that fails to recognize this has ceased to progress. No one not in direct touch with the soap industry and related industry can have any adequate idea of the multiplicity of chemical problems involved. The chemist who views great accomplishments in any field is inspired with a confidence that spurs him on to greater accomplishments in his own field. No matter how far afield the soap chemist may go in either the realm of organic or inorganic chemistry, there are always new and valuable things beyond and within reach if he can see where to grasp.

CHAPTER XXII

THE RELATION OF CHEMISTRY TO WATER SUPPLIES

W. W. Skinner

Assistant Chief, Bureau of Chemistry

The three most vital necessities in the life of man are air, food, and water. Not only his comfort and well-being, but indeed his very existence depend upon an adequate supply of these necessities. The adequacy of each is determined by its purity or quality as well as by its quantity. The pollution or contamination of any one of them is a serious disadvantage in the struggle for existence. The progress which man has made in securing pure air, pure food, and pure water has been due chiefly to the science of chemistry. In this chapter we shall consider how chemistry is employed to reclaim vast supplies of water which in its untreated condition is unfit for industrial purposes or for human consumption.

Water is a chemical compound formed by the chemical union of the gas hydrogen (H) with the gas oxygen (O) in the proportion of two volumes of hydrogen to one volume of oxygen, the chemical symbol being H_2O. The origin of water is the water vapor of the earth's atmosphere, the various physical forms of which are familiar to all as clouds, mists, dew, rain, snow, hail, and ice. The question may well be asked, "Whence came originally this water vapor in our earth's at-

mosphere?'' We must frankly admit that we do not know. According to the nebular theory of La Place, the earth as we know it has resulted from the cooling and contraction of a vast mass of exceedingly hot gaseous matter, in which water vapor probably did not exist but in which were present in the gaseous phase the necessary elements to form water, that is, hydrogen and oxygen. As the nebular mass cooled, water vapor was formed by the chemical reaction of these two constituents, and condensed to form water. The alternate vaporization and condensation of this water assisted materially in the cooling of the mass. Thus, water played a vital and perhaps a determining part in preparing the earth as we now know it and fitting it for the habitation of the vegetable and animal kingdoms. It has been said that the preparation of the earth for life was a contest between the great forces represented by fire and water, in which contest water was victorious.

Water for domestic consumption and industrial uses is derived principally from the following: rain, snow, surface waters, rivers, springs, and deep wells. The source of all these supplies is the condensed water vapor of the atmosphere. Theoretically, the condensation of this vapor produces pure water, but its pollution begins at once, or perhaps in the very act of formation, since the rain may dissolve or hold in suspension many gaseous, liquid, or solid impurities of organic or inorganic origin, which may be present in the atmosphere. Such impurities, including carbonic acid, sulfurous acid, chlorides, and ammonia, are especially prevalent in the atmosphere over cities and industrial works. As a greater variety of substances will dissolve in water than in any other solvent, water is called the universal solvent. When deposited on the

earth in the form of rain, it immediately begins to dissolve organic or inorganic substances through or over which it passes. Therefore, the character of the mineral matter dissolved in water depends upon the geological formation over which the water passes. By the action of water the face of the earth is modified and altered. The rocks and minerals precipitated from water, including marble, potash salts, common salt, gypsum, and minerals containing the heavy and precious metals, are very valuable to mankind, but when water itself is desired for use all dissolved and suspended impurities are generally objectionable and undesirable. The following is a fairly comprehensive outline of such impurities:

IMPURITIES IN WATER*

- 1. SUSPENDED MATTER
  - Inorganic or mineral — Sand, clay, and various pulverized minerals.
  - Organic
    - Animal: Living microscopic animals, dead fish and pieces thereof; feathers from birds, etc.; decayed animal refuse; manufacturing wastes, such as wool scourings, blood from slaughterhouses, etc.; excrement from sewers, etc.
    - Vegetable: Dried leaves, grass, and flowers, decayed wood, peaty matter; algæ and other plant life, including bacteria; wastes from cotton, silk, and linen mills, and from distilleries, etc.
- 2. DISSOLVED MATTER
  - Gaseous — Carbon dioxide. Hydrogen disulfide.
  - Solid
    - Inorganic mineral matter, including common salt, limestone, etc.
    - Organic — Animal (see above) Vegetable (see above)

*Water Supply and Irrigation Paper 79, U. S. Geological Survey.

The impurities in water are classed according to the purpose for which the water is to be used. For industrial purposes, such as the production of steam, the tanning of leather, the production and dyeing of textiles, and for laundry and household purposes other than drinking, the mineral impurities are of most importance, while for drinking purposes the dissolved

mineral matter, if it is of an ordinary type and present in ordinary amounts, is of secondary importance to organic impurities, since the latter represent a type of pollution which may be directly related to the dissemination of disease. Certain diseases, such as typhoid fever and cholera, which are among the great scourges of the human race, may be caused by polluted water.

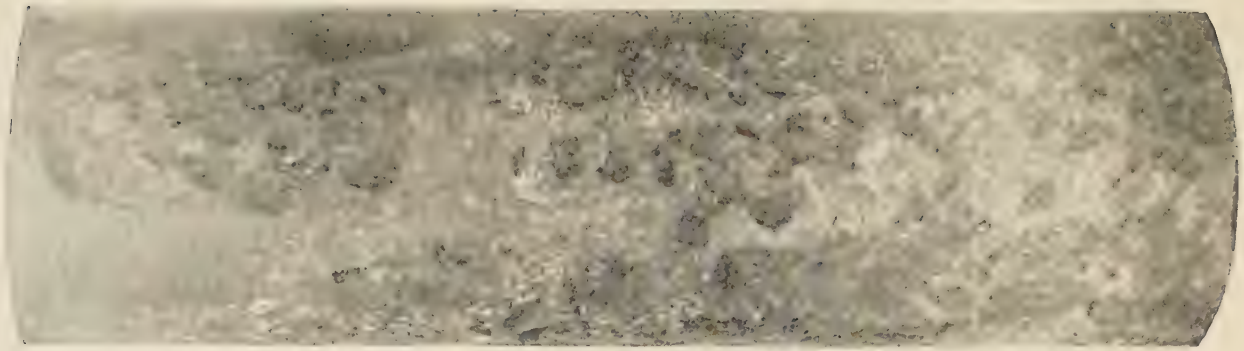
Since the contamination of water begins as soon as the water vapor of the atmosphere is condensed, we cannot expect to obtain pure water from natural sources. It is therefore incumbent upon us to call to our aid those sciences which may eliminate or reduce the impurities to a degree which produces a supply suitable for our purposes. In this effort chemistry plays a leading part.

Water Softening

As more water is used in the industries in the production of steam for power purposes than in any other way, the impurities which interfere with the production of steam or add to the cost of its production are of great industrial importance. A portion of the mineral matter dissolved in surface and ground water is precipitated when the water is boiled, and this deposit forms a scale which insulates the boiler or the tubes, causing a very material loss in heat. It has been estimated that a scale of one-quarter inch in thickness on the walls or tubes of a boiler will require 50 per cent additional fuel. The mineral matter which causes the most difficulty in this particular is the carbonates of calcium and magnesium and the sulfate of calcium. These salts, among others, are referred to as the "hardness" of the water. If the salts are largely

bicarbonates of these elements, the water is termed "temporarily" hard, meaning thereby that the salts can be largely precipitated by boiling and thus removed without causing the formation of a hard scale in the boiler. Sulfate of calcium is not removed by boiling the water, therefore this constituent together with certain other salts is known as "permanent hardness." Sulfate of calcium forms a porcelain-like scale that is removed from boilers only with the greatest difficulty. The salts which cause hardness are a tremendous disadvantage in the use of water for other industrial purposes, such as tanning, dyeing, and paper making. Especially in the use of water for laundry purposes are these salts a disadvantage and it is in this connection that the first attempt was made to counteract their effect by chemical means.

The process of removal by appropriate chemicals of those salts causing "hardness" is termed "water softening." The laundress by the river in the early days, who used wood ashes and soap to cleanse and whiten her clothes, was applying to her problem chemical principles of water softening which in recent times have developed into immense industrial importance. Dr. Thomas Clark, an English chemist, by the use of lime developed the first rational system of water softening treatment for removing calcium and magnesium carbonates. Later another chemist, Dr. J. H. Porter, developed the soda ash treatment of water to reduce the permanent hardness. Subsequently, the two systems were combined, and when necessary the two treatments are applied simultaneously. The Porter-Clark process, developed and perfected, is today used to soften billions of gallons of water annually. Not only is water softened for industrial use, but in many places throughout the Middle West and Far



Courtesy, Union Pacific System

Action of Water on Boiler Tube.

West it is found necessary or desirable to treat by these combined means the only water available for many cities, in order to produce an acceptable public supply. For the removal of the salts causing temporary hardness we depend upon the reaction of calcium hydroxide ($Ca(OH)_2$) with calcium carbonate ($CaCO_3$) in a solution of water (H_2O) and carbon dioxide (CO_2). The equation is as follows: $CaCO_3 + CO_2 + Ca(OH)_2 = 2CaCO_3 + H_2O$. The solution being deprived of carbon dioxide, the calcium carbonate can no longer remain in solution and is largely precipitated and may be removed by filtration. The reaction with magnesium salts is similar, except that sufficient lime must be added to convert the magnesium carbonate ($MgCO_3$) into magnesium hydroxide ($Mg(OH)_2$), which also is insoluble. The equation is as follows: $MgCO_3 + Ca(OH)_2 = Mg(OH)_2 + CaCO_3$. The permanent hardness may be removed with sodium carbonate (Na_2CO_3, washing soda or soda ash), as shown in the following equation:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

In the combined Porter-Clark process the calcium carbonate and magnesium hydroxide, being insoluble, may be removed by filtration; the sodium sulfate remaining in the solution is not scale-forming and is relatively unobjectionable.

Clarification of Water

Aluminium sulfate and iron sulfate (ferrous) are widely employed to assist in the clarification of water. The alum treatment of water was introduced and developed about the same time as the Porter-Clark softening process, although the use of alum for purposes

of clarification of water is much older, since it is a matter of record that the Chinese from the earliest times have treated water to be used in paper making with alum in order to remove the turbidity and undesirable coloring matter. When alum or aluminium sulfate ($Al_2(SO_4)_3$) is added to water which contains the requisite amount of alkalinity, the sulfate is decomposed, and a flocculent, gelatinous precipitate of aluminium hydroxide, $Al(OH)_3$ is formed, according to the following equation: $Al_2(SO_4)_3+3CaCO_3+3H_2O=3CaSO_4+3CO_2+2Al(OH)_3$. The flocculent precipitate, known in the water purification plant as the "floc," clarifies the water by entangling in the jell-like mass of aluminium hydroxide the suspended or colloidal matter which causes turbidity, thus permitting its removal by sedimentation or by filtration. It reacts also with the soluble coloring matter, which at the same time is removed. The "floc," moreover, drags down with it a large part of the bacterial contamination, thus assisting in purifying the supply for drinking purposes, since the "floc" materially aids in the subsequent filtration of the water.

The softening and clarification of water with chemicals is a technical operation that requires care and skill in order that just the right quantities of materials may be used and that no excess of alum or other undesirable material remain in the water delivered for consumption.

Treatment of Water with Disinfectants
Copper Sulfate

The next real advance made in this country in the protection and purification of water supplies for domestic purposes was the development of the copper

sulfate treatment, the great economic importance of which was pointed out by Drs. Moore and Kellerman, of the Bureau of Plant Industry, U. S. Department of Agriculture, in 1904. In order that a sufficient supply of potable water may be always available for towns and cities, it is usually necessary to provide large storage reservoirs. The storage of water, however, leads sometimes to difficulties, due to the growth of algæ or other vegetation, which either as living organisms or as dead and decaying matter produce disagreeable odors and tastes which at times are of such a character as to make the water unfit for domestic use. These low forms of vegetable life, however, are very susceptible to salts of copper, the authors referred to above having found that one part of copper sulfate to ten million parts of water is sufficient to kill some types of algæ, and one part in one million parts of water is sufficient to kill most of the common types upon which experiments were made. The introduction of this method of treating water stored for drinking purposes aroused some opposition because of the possible harmful effect of copper salts upon persons consuming treated water. Ample evidence has since accumulated, however, to prove that the grounds for fear were not well founded and to assure the public that with the proper supervision (and it may be well to repeat what has been said before, that no chemical treatment of water, especially for domestic purposes, should be permitted without such supervision) no harmful effects will result from a proper treatment of water with copper sulfate. The copper salt is added in very minute amounts only, a dose in excess of one part per million being seldom used. Furthermore, copper sulfate when added to the water in a reservoir is rapidly decomposed and

precipitated, so that only a small portion of the amount added probably ever reaches the public water mains. The entire amount added, if not in excess of one part per million, would not compare unfavorably with the copper content of some of our well-known foods, as may be seen from the following data:

Copper in Foods

	Parts per million
Almonds	36.8
Cocoa	47.0
Egg Yolk	5.6
Egg White	7.2
Figs	15.1
Grapes	1.0
Milk	1.6
Oatmeal	4.2
Potatoes	2.8

The algæ and other growths which produce disagreeable odors and tastes require sunlight for their development; hence, their development is most rapid at the edges or in the shallow bays of a reservoir. If careful inspection of such reservoirs is maintained, the treatment of these shallow portions with copper sulfate may be all that is required to keep in check the undesirable growths.

Germicidal Properties of Chlorine and Its Compounds

The epoch-making advancement in the purification of water by chemical means was the development of the chlorine treatment, which now assures a fairly certain nondisease-producing water supply to those cities and towns in America and in Europe where it is employed. The chlorine treatment of water sup-

plies did much to protect the troops engaged in the World War from the scourge of typhoid fever, which in every previous great war competed with the battle fields in destroying troops. The sole purpose of using chlorine in the treatment of a water supply is to destroy those organisms which produce disease in man, the principal culprit so far as American water supplies are concerned being the organism which produces typhoid fever.

Sewage Disinfection

The use of chlorine and chlorine compounds was first developed to disinfect sewage. One of the first electrolytic plants to be installed for this purpose was erected near London in 1889. The first plant in this country designed for the treatment of sewage with chlorine was at Brewster, N. Y., where, in 1893, a small plant was erected to protect the water of Croton Lake, which supplied New York City with water. From 1890 to 1900 much attention was given in England and on the continent to the possibilities of chlorine compounds in the treatment of both sewage and water. In 1907, Kellerman, Pratt, and Kimberley, of the U. S. Department of Agriculture, in coöperation with the Ohio State Board of Health, reported on chlorination experiments for purification of sewage at Lancaster, Ohio, showing a complete removal of the colon bacillus (fecal organisms) by such treatment.

Earle B. Phelps contributed materially to the advancement of the science of sewage and water treatment by chlorine in the reviews of previous works, to which he directed attention in 1906, and in his demonstrations of the great economic possibilities of chlorine as an effective disinfecting agent.

Houston and McGowan, of the English Royal Com-

mission on Sewage Disposal, in 1905 were perhaps the first to use hypochlorite in the treatment of the reservoirs and distribution systems for water at Lincoln, England, which having become seriously infected with typhoid bacilli, caused a severe epidemic of this disease. From this beginning the process of chlorination rapidly progressed. In 1908 the first large installation in this country for the chlorination of water was erected by G. A. Johnson, at the Union Stock Yards in Chicago, with very gratifying results. The first large installation for the treatment of a city supply was at Boonton, N. J., where Johnson and Leal erected a plant for the treatment of about forty million gallons of water per day, the supply of Jersey City. The water was treated with calcium hypochlorite, the amount being finally adjusted so that available chlorine at the rate of only about two-tenths part per million was used and found to be effective. This installation led to a famous law suit, which directed public as well as wider scientific attention to this new method of chemical water purification. During the trial it was satisfactorily proved that the method is efficacious and that with reasonable care no unfavorable results are to be anticipated from its use. Since that date the development in the use of chlorine in the purification of water has been remarkably rapid.

Liquid chlorine is chlorine gas liquefied by increase of pressure and decrease of temperature. It is a heavy, yellowish liquid which evolves reddish fumes when exposed to the air. It is supplied in cylindrical pressure tanks of steel equipped with a valve for releasing the contents. While liquid chlorine is now most widely employed in the chlorine treatment of water, formerly other compounds of chlorine were used

largely and they are used at the present time to a limited extent.

The effectiveness of both calcium hypochlorite (bleaching powder) and sodium hypochlorite is due to the action of chlorine. Calcium hypochlorite ($Ca(OCl)_2$) is a moist solid, manufactured by passing chlorine gas into slaked lime. The commercial product contains from 30 to 38 per cent of available or active chlorine. Bleaching powder is prepared for use by mixing it with water and separating the insoluble matter (mostly lime), which settles in the form of a sludge. The clear solution which is obtained is diluted with water to the proper strength for use.

Sodium hypochlorite (NaClO) is made in different strengths by electrolyzing a solution of sodium chloride (common salt). It comes in the form of a solution which can be diluted for use.

Effect of Water Treatment on Public Health

In the effective treatment of water by chlorine compounds, the dose should vary according to the amount of matter to be oxidized in the water, since Ellms has pointed out that the rate at which sterilization proceeds varies inversely with the amount of readily oxidizable matter present in the water. When such matter is present in an amount to require relatively large amounts of chlorine, for example, as much as two to five parts per million, before there is present sufficient residual chlorine available to produce the necessary bactericidal effect, difficulties may arise from disagreeable odors or tastes, due to the formation of organic compounds of chlorine, some of which are notoriously objectionable. In such cases the water must be treated by filtration or other means before the chlorine is added. It is now recognized that chlorination

in most cases is an adjunct to water purification, and in most plants it supplements and follows other treatments. Some idea of the effectiveness of the treatment of public water supplies by chlorine and chlorine compounds and what it means in the health of the nation may be gained by a comparison of the death rate in certain cities before and after the treatment of their water supplies by chlorine. The table on page 392 gives some interesting data.

It will be noted that the death rate from typhoid was reduced in numerous instances more than 70 per cent. It is believed that this reduction is due largely to the chlorine treatment, although it is recognized that other factors may have had some influence. It has, furthermore, been observed that in addition to the decrease of a special disease the general health in a community may be improved following the purification of an infected water supply.

In the above discussion we have considered only the most outstanding and widely used methods for the chemical purification of water. There are many other chemical or semichemical processes for treating water supplies, including the use of ozone, ultra-violet rays, tincture of iodine, base-exchanging filters, and preheaters. However, a relatively small portion of our water supplies are treated by these latter processes, although some of them will undoubtedly play an important role in water purification in the future. A few brief statements regarding them may not be out of place.

Ozone is a gas which is an active modification of oxygen. It has a bactericidal action and leaves no objectionable substances in the water which has been treated by it. There is some doubt as to whether or not ultra-violet ray treatment should be classed as a

chemical process. Ultra-violet rays are bactericidal, and clear, uncolored water can be rendered sterile or nearly so by bringing it in contact with the rays. Tincture of iodine is not employed on a large scale for treating water, but it is a good thing for campers and travelers to know that if one drop of ordinary tincture of iodine (7 per cent strength) is mixed with one quart of contaminated water, the water so treated will usually be safe for drinking purposes after thirty minutes. Base-exchanging filters are employed, not to sterilize water, but to soften it. The filtering medium possesses the property of removing the hardening constituents, namely, iron, calcium, and magnesium, from the water and replacing them with equivalent amounts of sodium. The actual amount of mineral matter dissolved in the water is not reduced, but the hardness is largely or entirely removed.

In thus affording a means of providing a safe and adequate water supply, chemistry renders a service of inestimable value to industry and to humanity. Thousands of dollars are saved annually and the conservation of natural resources and of human energy is made possible. Human lives are saved and sickness and the resulting incapacities are prevented, thereby conserving the most important asset of a nation—the public health.

READING REFERENCES

Christie. Water, Its Purification and Use in the Industries.
Coles-Finch. Water, Its Origin and Use.
Collet. Water Softening and Purification.
Hazen. Clean Water and How to Get It.
Lewes. Air and Water.
Mason. Water Supply.
Race. Chlorination of Water.
Richards and Woodman. Air, Water, and Food.
Rideal. Water and Its Purification.
Thresh and Beale. The Examination of Waters and Water Supplies.
Government Publications: Bureau of Plant Industry. Bulletins 64 and 115.
The Military Surgeon, 1922, 51, 661.

EFFECT OF CHLORINATION ON TYPHOID RATES

Typhoid Death Rate per 100,000 Population

Order in Size	City	Population (1920)	Before Using Period	Before Using Rate	After Using Period	After Using Rate	Percentage Reduction
1	New York, N. Y.	5,620,048	1906-10	13.5	1916-22	2.9	79
2	Chicago, Ill.	2,701,705	"	15.7	"	1.9	88
3	Philadelphia, Pa.	1,823,779	"	41.4	"	4.5	89
4	Detroit, Mich.	993,678	"	21.9	"	7.5	66
5	Cleveland, Ohio	796,841	"	15.9	"	4.0	75
6	St. Louis, Mo.	772,897	"	16.3	"	6.3	61
8	Baltimore, Md.	733,826	"	35.4	"	9.2	74
9	Pittsburgh, Pa.	588,343	"	66.8	"	7.7	88
11	Buffalo, N. Y.	506,775	"	23.1	"	6.8	71
13	Milwaukee, Wis.	457,147	"	27.8	"	5.6	80
16	Cincinnati, Ohio	401,247	"	30.9	"	3.5	89
18	Minneapolis, Minn.	380,582	"	31.9	"	4.2	87
19	Kansas City, Mo.	324,410	"	36.4	"	10.8	70
20	Seattle, Wash.	315,312	"	24.8	"	3.2	87
21	Indianapolis, Ind.	314,194	"	29.8	"	9.1	69
22	Jersey City, N. J.	298,103	"	12.6	"	4.2	67
25	Denver, Colo.	256,491	"	40.0	"	6.0	85
28	Columbus, Ohio	237,031	"	41.6	"	5.8	86
29	Louisville, Ky.	234,891	"	52.9	"	11.2	79
34	Omaha, Nebr.	191,601	"	41.1	"	5.1	88
38	Richmond, Va.	171,667	"	35.4	"	8.0	77
60	Albany, N. Y.	113,344	"	17.3	"	6.6	62

Data compiled from:

1. Bureau of the Census Reports:
   (a) Mortality Statistics (1919), p. 21.
   (b) Mortality Statistics (1922), p. 25.
   (c) Vol. I (1920), Population, pp. 78 and 80.
   (d) General Statistics of Cities (1915), pp. 43-45.
2. Municipal Journal, Vol. XLII, March 22, 1917, p. 404.